New Photosensitive Polymers: Synthesis and Free Radical Polymerization of Oxypyridinium and Oxyisoquinolinium Functionalized Methacrylate and Styrene Derivatives

Verena Görtz and Helmut Ritter*

Johannes Gutenberg-Universität Mainz, Institut für Organische Chemie, Duesbergweg 10-14, 55128 Mainz, Germany

Received October 9, 2001; Revised Manuscript Received February 20, 2002

ABSTRACT: Polymerizable hydroxypyridinium and hydroxyisoquinolinium salts **1a**−**4a**, **2d**, and **3d** have been prepared from vinylbenzyl chloride or glycidyl methacrylate and 3-hydroxypyridine (**2**), 4- or 5-hydroxyisoquinoline (**1**, **3**), and 8-hydroxyquinoline (**4**). Radical homo- and copolymerization with styrene or methyl methacrylate of the salts **1a**−**3a**, **2d**, and **3d** produced (co)polymers **1e**, **2e**, **2f**, **3f**, **1g**, **2g**, **2h**, and **3h**. The photosensitive dipolar oxypyridinium or oxyisochinolinium betaine structures were generated in solutions with triethylamine from the low molecular weight and polymeric salt precursors. For the model compounds **1b**−**4b** and (co)polymers **1e**, **2e**, **2f**, **3f**, **1g**, **2g**, **2h**, and **3h**, the degradation of the longest wavelength absorption of this betaine structure was detected during UV irradiation. UV irradiation of the model compound *N*-benzyl-4-hydroxyisochinolinium chloride (**1b**) in the presence of triethylamine produced the expected aziridine type structure **1k** by intramolecular cyclization.

Introduction

We have reported the synthesis and photochemical behavior of polymers with dipolar mesoionic and nitron functions as side groups or within the main chain.[1−6] UV irradiation of these highly polar dipoles leads to much less polar products via an intramolecular disrotatoric cyclization reaction.[7] This ring closure changes the physical properties of polymeric materials including solubility, absorption of UV light, film thickness, and refractive index.[8]

We now extended our studies on photosensitive polymers with pyridiniumolates and (iso)quinoliniumolates as photoisomerizable dipolar groups.

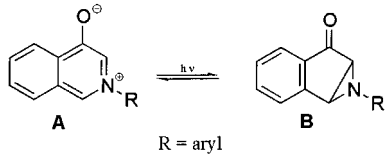
Katritzky's studies focused on the thermally induced dipolar cycloaddition reactions of various pyridiniumolates with olefins,[9−14] 1,3-dienes,[11−14] and ketenes[15] and also on dimerization reactions.[12,13,16] Upon irradiation, this type of betaine forms dimers or bicyclic aziridines[17] via intermolecular or intramolecular ring closure. The isoquinolinium series also undergo thermal dipolar cycloadditions.[18−20] Moreover, Hansen and Undheim reported[21] the reversible valence isomerism between the *N*-aryl-4-oxyisoquinolinium betaine **A** and the *N*-aryl bicyclic aziridine **B** upon irradiation as shown in Scheme 1.

This paper reports for the first time the synthesis and (co)polymerization of styrene and methacryloyl substituted 3-hydroxypyridinium, 4- and 5-hydroxyisoquinolinium, and 8-hydroxyquinolinium salts. Furthermore, the photochemistry of the free betaine structure, generated by alkaline treatment of the salt precursors, is discussed.

Experimental Section

Materials and Methods. The materials benzyl chloride (Fluka, 99%), vinylbenzyl chloride (Fluka, 95%, mixture of isomers (70% para and 30% meta)), 3-hydroxypyridine (Fluka, 98%), 5-hydroxyisoquinoline (Aldrich, 90%), 8-hydroxyquinoline (Fluka, 99%), glycidyl methacrylate (Fluka, 97%), potassium peroxodisulfate (Fluka, 99%), AIBN (Fluka, 98%), and ion-exchange resin Amberlite IRA-410 (Fluka, 20−40 mesh) were used as received. 4-Hydroxyisoqouinoline was synthesized according to the literature.[22,23] Technical solvents, styrene (Acros Organics, 99%), and MMA (Fluka, 99%) were distilled before use. Solvents of p.a. quality were purchased from Riedel de Haen. The TLC analysis was carried out using silica gel plates (60 F 254) purchased from Merck. The spots were visualized by UV fluorescence quenching and by development with iodine. For flash-chromatography silica gel with 30 to 60 μm particle size purchased from Baker was used. Melting points were determined with an instrument from Büchi and are uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded (at room temperature) on a Bruker AC 200 using the signal of the deuterated solvent as lock and internal standard for chemical shift data in the δ-scale relative to TMS. For infrared spectroscopy a Nicolet FT-IR 5DXC (DTGS detector) or a 5SXB (MCT detector) was used. UV−vis spectra were performed on a Zeiss-MCS320/MCS340 diode array spectrometer. Field desorption (FD) mass spectrometry was done using a Finnigan MAT 95. Elementary analysis was carried out in the analytical laboratory of the institute of organic chemistry at the University of Mainz. Molecular modeling calculations were implemented using PC Spartan Pro 1.07; the density functional theory (DFT) method pBP/DN* was used for geometry optimizations and energy calculations.

Scheme 1



Synthesis of Hydroxypyridinium and Hydroxy(iso)-quinolinium Chlorides. *N*-Benzyl-3-hydroxypyridinium Chloride (2b). A solution of benzyl chloride (12.0 g, 124 mmol) and 3-hydroxypyridine (8.0 g, 62 mmol) in dry acetone (100 mL) was stirred for 48 h at room temperature. The white precipitate was collected, and from the filtrate, the solvent was evaporated. More crude product separated after the addition of acetonitrile. The product was recrystallized from acetonitrile. Yield: 16.2 g (76%), colorless crystals. Mp: 154−156 °C (lit.:[25] 158−159 °C).

^{1}H NMR (DMSO-d_6): δ [ppm] = 12.50 (br s, 1H, O*H*), 8.83 (s, 1H, H-2), 8.72 (d, 1H, $J_{5,6}$ = 5.9 Hz, H-6), 8.11 (dd, 1H, $J_{2,4}$

10.1021/ma011750b CCC: $22.00 © 2002 American Chemical Society
Published on Web 04/27/2002

= 2.2 Hz, $J_{4,5}$ = 8.5 Hz, H-4), 7.95 (dd, 1H, $J_{5,6}$ = 5.9 Hz, $J_{4,5}$ = 8.5 Hz, H-5), 7.56−7.03 (m, 5H, ar-H), 5.78 (s, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ [ppm] = 157.51 (C-3), 134.32 (*C*−CH$_2$), 135.32, 132.62, 131.71, 129.15 (C-2, C-4, C-5, C-6), 129.02 (ar-*C*H-para), 128.65, 128.60 (ar-*C*H-ortho, ar-*C*H-meta), 62.97 (*C*H$_2$).

***N*-Vinylbenzyl-3-hydroxypyridinium Chloride (2a).** Vinylbenzyl chloride (15.2 g, 0.1 mol) was added to a solution of 3-hydroxypyridine (9.5 g, 0.1 mol) and a small amount of hydroquinone in dry acetone (70 mL). After the reaction was stirred for 48 h at room temperature under exclusion of light and moisture, the solvent was removed by evaporation. The product crystallized on addition of acetonitrile and a grain of *N*-benzyl-3-hydroxypyridinium chloride (**2b**) to the remaining oil. Yield: 17.4 g (70%), colorless, hygroscopic crystals. Mp: 112 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 12.50 (br s, 1H, O*H*), 8.84 (d, 1H, $J_{5,6}$ = 5.9 Hz, H-6), 8.70−8.73 (m, 1H, H-2), 8.11 (d, 1H, $J_{4,5}$ = 8.5 Hz, H-4), 7.93 (dd, 1H, $J_{5,6}$ = 5.9 Hz, $J_{4,5}$ = 8.5 Hz, H-5), 7.70−7.39 (m, 4H, ar-H), 6.72 (dd, 1H, J_{cis} = 10.7 Hz, J_{trans} = 17.7 Hz, C*H*=CH$_2$), 5.87 (dd, 1H, J_{gem} = 3.2 Hz, J_{trans} = 17.7 Hz, CH=CHH_{trans}), 5.77 (s, 2H, N$^+$−CH_2), 5.30 (dd, 1H, J_{gem} = 3.2 Hz, J_{cis} = 10.7 Hz, CH=CHH_{cis}).

^{13}C NMR (DMSO-d_6): δ [ppm] = 157.48 (C-3), 137.95, 137.88 (ar-*C*−CH=CH$_2$), 135.86, 135.76 (*C*H=CH$_2$), 135.33, 132.66, 131.67, 129.38 (C-2, C-4, C-5, C-6), 134.75, 133.78, 129.09, 128.64, 128.12, 126.97, 126.71, 126.50 (ar-*C*H), 115.52, 115.44 (CH=*C*H$_2$), 62.84, 62.67 (N$^+$−*C*H$_2$).

IR (KBr): [cm^{-1}] = 3371 (br, O−H), 3056, 3029 (ar C−H), 2979, 2829 (aliph C−H), 2727,2614, 2510 (pyr O−H), 1628, 1584, 1510 (C=C, C=N), 994, 919 (CH=CH$_2$ out of plane), 807, 764 (ar C−H out of plane), and 1447, 1266, 1148, 1032.

MS (FD): *m*/*z* (%) = 212 (3) [M$^+$ − Cl], 211 (100) [M$^+$ − HCl].

Anal. Calcd for $C_{14}H_{14}NOCl$ (247.72): C, 67.88; H, 5.70; N, 5.65; (O), 6.46; Cl, 14.31. Found: C, 67.53; H, 6.02; N, 5.58; (O), 6.75; Cl, 14.12.

***N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-3-hydroxypyridinium Chloride (2d).** *N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-3-oxypyridinium betaine (**2c**, 2.90 g, 12 mmol) was dissolved in water (10 mL) and stirred. Half concentrated aqueous acid chloride was slowly added until a pH of 1 was reached. After distillation under reduced pressure the residue was purified by flash chromatography (chloroform/ methanol, 1:1). Yield: 2.41 g (69%), colorless solid. Mp: 134−137 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 8.55 (s, 1H, H-2), 8.47−8.45 (m, 1H, H-6), 8.05−8.01 (m, 1H, H-4), 7.90−7.87 (m, 1H, H-5), 6.11 (s, 1H, C=CHH_{cis}), 5.70 (s, 1H, C=CHH_{trans}), 4.76 (d, 1H, J_{gem} = 12.2 Hz, N$^+$−CHH_a), 4.48 (br. s, 1H, N$^+$−CHH_b), 4.15 (br. s, 3H, C*H*−OH, CH_2−O), 1.88 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6): δ [ppm] = 166.26 (*C*=O), 157.37 (C-3), 135.66, 133.60, 131.45, 127.76 (C-2, C-4, C-5, C-6), 135.46 (*C*=CH$_2$), 126.34 (C=*C*H$_2$), 67.68 (*C*H−OH), 65.49 (*C*H$_2$−O), 63.00 (N$^+$−*C*H$_2$), 17.95 (*C*H$_3$).

IR (KBr): [cm^{-1}] = 3321 (br, O−H), 3063, 3004 (ar C−H), 2730, 2610, 2470 (pyr O−H), 1714 (C=O), 1635, 1589, 1512 (C=C, C=N), 1168 (C−OR) and 1460, 1310, 1252, 1127, 1032, 957, 812, 686.

MS (FD): *m*/*z* (%) = 238 (42) [M$^+$ − Cl], 237 (100) [M$^+$ − HCl], 151 (47).

***N*-Benzyl-5-hydroxyisoquinolinium Chloride (3b).** 5-Hydroxyisoquinoline (0.50 g, 3.4 mmol) and benzyl chloride (0.44 g, 3.4 mmol) were dissolved in dry ethanol (20 mL) and stirred for 4 days at room temperature. The solvent was evaporated and the remaining orange-red solid was purified by flash chromatography (methanol). Yield: 660 mg (70%), red solid. Mp: 132−134 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 9.67 (s, 1H, H-1), 8.39 (d, 1H, $J_{3,4}$ = 6.3 Hz, H-3), 8.18 (d, 1H, $J_{3,4}$ = 6.3 Hz, H-4), 7.67−7.40 (m, 6H, ar-H, H-7), 6.93 (d, $J_{6,7}$ = 7.3 Hz, H-6), 6.73 (d, $J_{7,8}$ = 8.3 Hz, H-8), 5.76 (s, 2H, CH_2).

IR (KBr): [cm^{-1}] = 3060, 3038 (ar C−H), 2959, 2897 (aliph C−H), 2790, 2730, 2610, 2589, 2557 (pyr O−H), 1636, 1603, 1587 (C=C, C=N), 749, 717 (ar out of plane), and 1458, 1394, 1353, 1285, 1036, 890, 798.

MS (FD): *m*/*z* (%) = 237 (18) [MH$^+$ − Cl], 236 (27) [M$^+$ − Cl], 235 (100) [M$^+$ − HCl], 145 (60) [5-hydroxyisoquinolinium$^+$].

***N*-Vinylbenzyl-5-hydroxyisoquinolinium Chloride (3a).** A solution of 5-hydroxyisoquinoline (1.0 g, 7 mmol), vinylbenzyl chloride (1.1 g, 7 mmol) and a small amount of hydroquinone in dry ethanol (30 mL) was stirred for 72 h. After evaporation of the solvent, the residue was purified by flash chromatography (methanol). Yield: 1.5 g (71%), red solid. Mp: 81 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 9.57 (d, 1H, $J_{1,3}$ = 2.4 Hz, H-1), 8.33 (d, 1H, $J_{3,4}$ = 6.8 Hz, H-3), 8.08 (t, 1H, $J_{7,6+8}$ = 9.3 Hz, H-7), 7.64−7.37 (m, 5H, ar-H, H-4), 6.76 (d, 1H, $J_{6,7}$ = 9.3 Hz, H-6), 6.71 (dd, 1H, J_{cis} = 11.2 Hz, J_{trans} = 18.0 Hz, C*H*=CH$_2$), 6.56 (d, 1H, $J_{7,8}$ = 8.3 Hz, H-8), 5.85 (dd, 1H, J_{gem} = 2.9 Hz, J_{trans} = 18.0 Hz, CH=CHH_{trans}), 5.71 (s, 2H, N$^+$−CH_2), 5.29 (dd, 1H, J_{gem} = 2.9 Hz, J_{cis} = 11.2 Hz, CH=CHH_{cis}).

^{13}C NMR (DMSO-d_6): δ [ppm] = 162.81 (C-5), 148.5, 148.36, 134.12, 133.41, 122.67, 118.90, 111.32, 111.24 (C-1, C-3, C-4, C-6, C-7, C-8), 137.91, 137.83 (ar-*C*−CH=CH$_2$), 135.91, 135.80 (*C*H=CH$_2$), 135.06 (ar-*C*−CH$_2$), 130.64, 130.12 (C-9, C-10), 129.47, 129.32, 128.92, 127.95, 126.68 (ar-*C*H), 115.61, 115.32 (CH=*C*H$_2$), 62.45, 62.25 (N$^+$−*C*H$_2$).

IR (KBr): [cm^{-1}] = 3390 (O−H), 3083, 3032, 3005 (ar C−H), 2500 (br, pyr O−H), 1628, 1573, 1503 (C=C, C=N), 991, 915 (CH=CH$_2$ out of plane), 848, 829, 793, 777 (ar C−H out of plane) and 1469, 1452, 1413, 1382, 1318, 1286, 1090, 760, 740, 713.

MS (FD): *m*/*z* (%) = 523 (89) [M$_2^+$ − 2HCl], 263 (41) [MH$^+$ − Cl], 262 (100) [M$^+$ − Cl], 261 (18) [M$^+$ − HCl], 144.8 (35) [5-hydroxyisoquinolinium$^+$].

***N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-5-hydroxyisoquinolinium Chloride (3d).** *N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-5-oxyisoquinolinium betaine (**3c**, 1.60 g, 5.6 mmol) was stirred in water (10 mL). When half concentrated aqueous acid chloride was slowly added until a pH of 1 was reached, the remaining solid dissolved and the red solution eventually turned to orange. After the addition of 200 mL of chloroform and vigorous shaking, the solid precipitated and concentrated at the interface. It was filtered off and washed with chloroform. Yield: 1.60 g (89%), light yellow solid. Mp: 184−186 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 11.73 (s, 1H, hetar-O*H*), 9.95 (s, 1H, H-1), 8.66 (d, 1H, $J_{3,4}$ = 6.8 Hz, H-3), 8.55 (d, 1H, $J_{7,8}$ = 9.8 Hz, H-8), 7.95−7.83 (m, 2H, H-7, H-6), 7.63 (d, 1H, $J_{3,4}$ = 6.8 Hz, H-4), 6.11 (s, 1H, C=CHH_{cis}), 5.88 (br s, 1H, CH−O*H*), 5.72 (s, 1H, C=CHH_{trans}), 4.95 (d, 1H, J_{gem} = 12.7 Hz, N$^+$−CHH_a), 4.62 (dd, 1H, J_{vic} = 8.5 Hz, J_{gem} = 12.7 Hz, N$^+$−CHH_b), 4.25 (m, 3H, C*H*−OH, CH_2−O), 1.90 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6): δ [ppm] = 166.27 (*C*=O), 153.15 (C-5), 150.23, 134.23, 132.18, 120.36, 120.04, 118.30 (C-1, C-3, C-4, C-6, C-7, C-8), 135.47 (*C*=CH$_2$), 128.04, 128.00 (C-9, C-10), 126.33 (C=*C*H$_2$), 67.60 (*C*H−OH), 65.62 (*C*H$_2$−O), 63.07 (N$^+$−*C*H$_2$), 17.95 (*C*H$_3$).

IR (KBr): [cm^{-1}] = 3365 (O−H), 3134, 3104, 3019 (ar C−H), 2990 (aliph C−H), 2760, 2675, 2609 (pyr O−H), 1715 (C=O), 1635, 1605, 1580, 1522 (C=C, C=N), 1189 (C−OR) and 1696, 1474, 1454, 1405, 1328, 1298, 1205, 965, 953, 791, 759.

MS (FD): *m*/*e* (%) = 288 (40) [M$^+$ − Cl], 287 (100) [M$^+$ − HCl].

Anal. Calcd for $C_{16}H_{18}NO_4Cl$ (323.77): C, 59.36; H, 5.60; N, 4.33; (O), 19.77; Cl, 10.95. Found: C, 58.68; H, 5.31; N, 4.35; (O), 20.80; Cl, 10.86.

***N*-Benzyl-4-hydroxyisoquinolinium Chloride (1b).** Benzyl chloride (300 mg, 2.4 mmol) was added to a solution of 4-hydroxyisoquinoline[22,23] (350 mg, 2.4 mmol) in DMF (7 mL). The orange solution was stirred for 72 h at room temperature, poured into water (100 mL), and extracted four times with dichloromethane (15 mL). The combined organic layers were washed twice with water, dried over magnesium sulfate, and evaporated. The residue was purified by flash chromatography (ethyl acetate/methanol, 1:1). Yield: 360 mg (55%), light yellow solid. Mp: 144−147 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 9.50 (s, 1H, H-3), 8.27 (d, 1H, $J_{7,8}$ = 7.8 Hz, H-8), 8.17 (d, 1H, $J_{5,6}$ = 8.3 Hz, H-5), 7.98−7.81 (m, 2H, H-6, H-7), 7.70 (s, 1H, H-1), 7.50−7.37 (m, 5H, ar-H), 5.69 (s, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ [ppm] = 153.54 (C-4), 140.37, 134.12, 131.47, 126.50, 121.86, 118.49 (C-1, C-3, C-5, C-6, C-7, C-8), 135.26 (ar-*C*−CH_2), 129.91, 129.39 (C-9, C-10), 129.18, 127.99, 126.95 (ar-*C*H), 63.47 (CH_2).

IR (KBr): [cm^{-1}] = 3061, 3031 (ar C−H), 2958, 2873 (aliph C−H), 2550 (pyr O−H), 1679, 1637, 1600, 1581 (C=C, C=N), 753, 706 (ar C−H out of plane) and 1471, 1456, 1416, 1379, 1286, 1131, 1074.

MS (FD): *m/z* (%) = 236 (12) [M^+ − Cl], 235 (100) [M^+ − HCl].

***N*-Vinylbenzyl-4-hydroxyisoquinolinium Chloride (1a).** *N*-Vinylbenzyl-4-hydroxyisoquinolinium chloride (**1a**) was prepared similarly to **1b** using 4-hydroxyisoquinoline[22,23] (2.50 g, 17 mmol) and vinylbenzyl chloride (2.60 g, 17 mmol) and adding some hydroquinone. Yield: 2.18 g (49%), light yellow solid. Mp: 133−135 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 13.06 (br s, 1H, O*H*), 9.77 (s, 1H, H-3), 8.37 (d, 1H, $J_{7,8}$ = 8.8 Hz, H-8), 8.28 (d, 1H, $J_{5,6}$ = 7.8 Hz, H-5), 8.13−7.98 (m, 2H, H-6, H-7), 7.72 (s, 1H, H-1), 7.51−7.38 (m, 4H, ar-H), 6.70 (dd, 1H, J_{cis} = 11.2 Hz, J_{trans} = 18.1 Hz, C*H*=CH_2), 5.89 (s, 2H, N^+−CH_2), 5.83 (d, J_{trans} = 18.1 Hz, CH=CHH_{trans}), 5.27 (d, J_{cis} = 11.2 Hz, CH=CHH_{cis}).

^{13}C NMR (DMSO-d_6): δ [ppm] = 153.55 (C-4), 140.29, 133.67, 131.31, 126.18, 121.84, 118.46 (C-1, C-3, C-5, C-6, C-7, C-8), 137.95 (ar-*C*−CH=CH_2), 135.79 (*C*H=CH_2), 135.20 (ar-*C*−CH_2), 129.89, 129.38 (C-9, C-10), 129.14, 127.96, 126.73 (ar-*C*H), 115.49 (CH=*C*H_2), 64.82 (N^+−*C*H_2).

MS (FD): *m/z* (%) = 523 (14) [M_2H^+ − 2HCl], 522 (18) [M_2^+ − 2HCl], 262 (21) [M^+ − Cl], 261 (100) [M^+ − HCl].

***N*-Benzyl-8-hydroxyquinolinium Chloride (4b).** A solution of 8-hydroxyquinoline (4.00 g, 27 mmol) and benzyl chloride (3.40 g, 27 mmol) in ethanol (30 mL) was stirred for 5 days at room temperature. The solvent was evaporated, and the remaining red, viscous oil crystallized from ethanol/ethyl acetate. Yield: 1.7 g (23%), yellow solid. Mp: 164−166 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 12.38 (s, 1H, O*H*), 9.57 (d, 1H, $J_{2,3}$ = 6.0 Hz, H-2), 9.25 (d, 1H, $J_{3,4}$ = 8.3 Hz, H-4), 9.01 (d, 1H, $J_{6,7}$ = 6.8 Hz, H-7), 8.14 (dd, 1H, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 8.3 Hz, H-3), 8.03 (dd, 1H, $J_{6,7}$ = 6.8 Hz, $J_{5,6}$ = 8.8 Hz, H-6), 7.88−7.66 (m, 4H, ar-H), 7.40 (d, 1H, $J_{5,6}$ = 8.8 Hz, H-5), 6.62 (s, 2H, CH_2).

IR (KBr): [cm^{-1}] = 3297 (O−H), 3043, 3009 (ar C−H), 2948, 2886 (aliph C−H), 2671, 2616, 2549 (pyr O−H), 1594, 1550, 1497 (C=C, C=N), 738, 697 (ar C−H out of plane) and 1452, 1378, 1368, 1319, 1312, 1247, 1158, 1133, 838, 815, 760.

MS (FD): *m/z* (%) = 236 (21) [M^+ − Cl], 235 (100) [M^+ − HCl].

Anal. Calcd for $C_{16}H_{14}NOCl$ (271.74): C, 70.91; H, 5.19; N, 5.15; (O), 5.89; Cl, 13.05. Found: C, 69.84; H, 4.70; N, 5.45; (O), 6.24; Cl, 13.77.

***N*-Vinylbenzyl-8-hydroxyquinolinium Chloride (4a).** *N*-Vinylbenzyl-8-hydroxyquinolinium chloride (**4a**) was prepared similarly to **4b** using 8-hydroxyisoquinoline (4.00 g, 27 mmol) and vinylbenzyl chloride (4.1 g, 27 mmol) and adding hydroquinone. The product crystallized on addition of a grain of **4b**. Yield: 2.20 g (27%), orange crystals. Mp: 129−132 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 12.39 (s, 1H, O*H*), 9.58 (d, 1H, $J_{2,3}$ = 5.9 Hz, H-2), 9.23 (d, 1H, $J_{3,4}$ = 8.3 Hz, H-4), 9.08 (d, 1H, $J_{6,7}$ = 6.8 Hz, H-7), 8.13 (dd, 1H, $J_{2,3}$ = 5.9 Hz, $J_{3,4}$ = 8.3 Hz, H-3), 8.03 (dd, 1H, $J_{6,7}$ = 6.8 Hz, $J_{5,6}$ = 8.8 Hz, H-6), 7.89−7.65 (m, 4H, ar-H), 7.39 (d, 1H, $J_{5,6}$ = 8.8 Hz, H-5), 6.67 (dd, 1H, J_{cis} = 11.2 Hz, J_{trans} = 17.6 Hz, C*H*=CH_2), 6.60 (s, 2H, N^+−CH_2), 5.79 (d, 1H, J_{trans} = 17.6 Hz, CH=CHH_{trans}), 5.23 (d, 1H, J_{cis} = 11.2 Hz, CH=CHH_{cis}).

IR (KBr): [cm^{-1}] = 3270 (O−H), 3043 (ar C−H), 2991 (aliph C−H), 1595, 1546, 1516 (C=C, C=N), 995, 916 (CH=CH_2 out of plane), and 1460, 1362, 1307, 1247, 1200.

MS (FD): *m/z* (%) = 523 (9) [M_2^+ − 2HCl], 262 (24) [M^+ − Cl], 261 (100) [M^+ − HCl].

Anal. Calcd for $C_{18}H_{16}NOCl$ (297.78): C, 72.60; H, 5.41; N, 4.70; (O), 5.37; Cl, 11.90. Found: C, 71.71; H, 5.06; N, 4.63; (O), 6.68; Cl, 11.92.

Synthesis of the Betaines. *N*-(2-Hydroxy-1-methacryloxypropyl-3)-3-oxypyridinium Betaine (2c). A solution of 3-hydroxypyridine (3.8 g, 40 mmol), glycidyl methacrylate (5.6 g, 40 mmol) and some hydroquinone in dry ethanol (50 mL) was stirred for 19 h. After the removal of the solvent, the oily, greenish residue crystallized during drying in a vacuum. The product was purified by flash chromatography (ethyl acetate/methanol, 1:2), which had to be done quickly as the product slowly hydrolyzed to *N*-(1,2-hydroxypropyl-3)-3-oxypyridinium betaine on the silica gel column. Yield: 7.4 g (78%), light green solid. Mp: 143−146 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 7.34−7.18 (m, 3H, H-2, H-6, H-5), 6.85 (d, 1H, $J_{4,5}$ = 8.3 Hz, H-4), 6.12 (s, 1H, C=CHH_{cis}), 6.04 (br s, 1H, CH−O*H*), 5.70 (s, 1H, C=CHH_{trans}), 4.34 (d, 1H, J_{gem} = 9.8 Hz, CHH_a-O), 4.08 (br s, 4H, N^+−CH_2, C*H*−OH, CHH_b−O), 1.89 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6): δ [ppm] = 170.45 (C-3), 169.45 (*C*=O), 138.53, 137.21, 129.71, 129.35 (C-2, C-4, C-5, C-6), 136.06 (*C*=CH_2), 128.06 (C=*C*H_2), 70.91 (*C*H−OH), 67.99 (*C*H_2−O), 65.74 (N^+−*C*H_2), 19.64 (*C*H_3).

IR (KBr): [cm^{-1}] = 3300 (vbr, O−H), 3050 (ar C−H), 2960, 2929 (aliph C−H), 1716 (C=O), 1637, 1594, 1568, 1502 (C=C, C=N), 1169 (C−OR) and 1456, 1365, 1027, 950, 813, 772, 685.

MS (FD): *m/z* (%) = 476 (21) [M_2H^+], 475 (100) [M_2^+], 238 (12) [MH^+], 237 (2) [M^+].

Anal. Calcd for $C_{12}H_{15}NO_4$ (237.26): C, 60.75; H, 6.37; N, 5.90; (O), 26.97. Found: C, 60.56; H, 6.47; N, 6.02; (O), 26.95.

***N*-Benzyl-3-oxypyridinium Betaine (2i).** An ion exchange column (100 mL ion-exchange resin Amberlite IRA-410, Cl^--form) was activated with 4 N aqueous sodium hydroxide solution and washed neutral with water. A solution of *N*-benzyl-3-hydroxypyridinium chloride (3.00 g, 13 mmol) in water (30 mL) was brought onto the column and eluted with water (300 mL). After removal of the solvent, the residue crystallized during drying in a vacuum. Yield: 2.7 g (98%), monohydrate, colorless hygroscopic crystals. Mp: 102−105 °C (lit.:[26] 107−111 °C).

^{1}H NMR (DMSO-d_6): δ [ppm] = 7.52−7.37 (m, 7H, ar-H, H-2, H-6), 7.25 (dd, 1H, $J_{5,6}$ = 5.4 Hz, $J_{4,5}$ = 9.3 Hz, H-5), 6.88 (dd, 1H, $J_{2,4}$ = 1.9 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 5.36 (s, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ [ppm] = 169.03 (C-3), 135.44 (ar-*C*−CH_2), 133.57, 132.68, 126.85, 120.79 (C-2, C-4, C-5, C-6), 128.71 (ar-*C*H-para), 128.87, 128.19 (ar-*C*H-ortho, ar-*C*H-meta), 62.13 (*C*H_2).

Anal. Calcd for $C_{12}H_{11}NO\cdot H_2O$ (203.23): C, 70.92; H, 6.44; N, 6.89; (O), 15.74; Found: C, 71.00; H, 6.78; N, 6.91; (O), 15.31.

***N*-Vinylbenzyl-3-oxypyridinium Betaine (2j).** *N*-Vinylbenzyl-3-oxypyridinium betaine (**2j**) was prepared similar to **2i** using *N*-vinylbenzyl-3-hydroxypyridinium chloride. It was dried to constant weight under reduced pressure but failed to crystallize. Yield: quantitative if regarded as the monohydrate, colorless very hygroscopic viscous oil.

^{1}H NMR (DMSO-d_6): δ [ppm] = 7.60−7.35 (m, 6H, ar-H, H-2, H-6), 7.24 (dd, 1H, $J_{5,6}$ = 5.4 Hz, $J_{4,5}$ = 8.8 Hz, H-5), 6.86 (dd, 1H, $J_{2,4}$ = 2.4 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 6.72 (dd, 1H, J_{cis} = 11.2 Hz, J_{trans} = 17.6 Hz, C*H*=CH_2), 5.85 (d, 1H, J_{trans} = 17.6 Hz, CH=CHH_{trans}), 5.33 (s, 2H, CH_2), 5.28 (dd, 1H, J_{gem} = 3.9 Hz, J_{cis} = 11.2 Hz, CH=CHH_{cis}).

IR (KBr): [cm^{-1}] = 3391 (br, O−H), 3088, 3064 (ar C−H), 2980 (aliph C−H), 1589, 1566, 1505 (C=C, C=N), 993, 917 (CH=CH_2 out of plane), 832, 765 (ar C−H out of plane) and 1649, 1462, 1371, 1342, 1029.

***N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-5-oxyisoquinolinium Betaine (3c).** *N*-(2-Hydroxy-1-methacryloyloxypropyl-3)-5-oxyisoquinolinium betaine (**3c**) was prepared similar to **2c** reacting glycidyl methacrylate (7 mmol) with 5-hydroxyisoquinoline (7 mmol) in ethanol (30 mL) for 42 h. The crude dark red product was purified by flash chromatography (methanol). A slow hydrolysis of the product started on the silica gel column. Yield: 0.9 g (45%), orange red solid. Mp: 162−165 °C.

^{1}H NMR (DMSO-d_6): δ [ppm] = 9.30 (s, 1H, H-1), 8.26 (d, 1H, $J_{3,4}$ = 6.8 Hz, H-3), 8.02 (d, 1H, $J_{3,4}$ = 6.8 Hz, H-4), 7.42 (dd, 1H, $J_{6,7}$ = 7.8 Hz, $J_{7,8}$ = 8.3 Hz, H-7), 6.78 (d, 1H, $J_{6,7}$ = 7.8 Hz, H-6), 6.55 (d, 1H, $J_{7,8}$ = 8.3 Hz, H-8), 6.14 (s, 1H, C=CHH_{cis}), 5.73 (s, 1H, C=CHH_{trans}), 4.70 (d, 1H, J_{gem} = 13.0 Hz,

$N^+-CH_aH_b$), 4.38 (d, 1H, J_{gem} = 13.0 Hz, $N^+-CH_aH_b$), 4.20 (m, 3H, $CH-OH$, CH_2-O), 1.91 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6): δ [ppm] = 169.52 (C=O), 167.42 (C-5), 151.46, 138.51, 134.46, 124.87, 123.58, 114.80 (C-1, C-3, C-4, C-6, C-7, C-8), 136.03 (C=CH_2), 132.55, 132.10 (C-9, C-10), 128.07 (C=CH_2), 70.72 ($CH-OH$), 68.11 (CH_2-OH), 65.68 (N^+-CH_2), 19.61 (CH_3).

IR (KBr): [cm^{-1}] = 3027 (ar C−H), 2960, 2926, 2884 (aliph C−H), 1716 (C=O), 1633, 1573, 1503, (C=C, C=N), 1160 (C−OR) and 1470, 1454, 1417, 1388, 1337, 1321, 1255, 1118, 1027, 953, 938, 851, 784, 750, 741.

MS (FD): m/z (%) = 288 (12) [MH^+], 287 (100) [M^+].

Anal. Calcd for $C_{16}H_{17}NO_4$ (287.31): C, 66.89; H, 5.96; N, 4.87; (O), 22.27. Found: C, 65.75; H, 5.84; N, 5.07; (O), 23.34.

***N*-Benzyl-5-oxyisoquinolinium Betaine (3i).** *N*-Benzyl-5-oxyisoquinolinium betaine (**3i**) was prepared similar to **2i** and **2j** using *N*-benzyl-5-hydroxyisoquinolinium chloride. Yield: 80% dihydrate, red violet solid. Mp: 91 °C.

^1H NMR (DMSO-d_6): δ [ppm] = 9.57 (s, 1H, H-1), 8.33 (d, 1H, $J_{3,4}$ = 6.5 Hz, H-3), 8.07 (d, 1H, $J_{3,4}$ = 6.5 Hz, H-4), 7.52−7.37 (m, 6H, ar-H, H-7), 6.74 (d, 1H, $J_{6,7}$ = 7.8 Hz, H-6), 6.54 (d, 1H, $J_{7,8}$ = 8.3 Hz, H-8), 5.70 (s, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ [ppm] = 167.92 (C-5), 147.49, 134.00, 127.83, 123.41, 119.42, 105.10 (C-1, C-3, C-4, C-6, C-7, C-8), 139.8 (ar-$C-CH_2$), 131.91, 130.35 (C-9, C-10), 129.04, 128.43 (ar-CH-ortho, ar-CH-meta), 128. 91 (ar-CH-para), 62.25 (CH_2).

IR (KBr): [cm^{-1}] = 3108, 3062, 3029 (ar C−H), 1623, 1579, 1503 (C=C, C=N), 742, 716 (ar C−H out of plane) and 1474, 1460, 1425, 1383, 1342, 1309, 1181, 1093, 853, 784.

MS (FD): m/z (%) = 236 (23) [MH^+], 235 (100) [M^+].

Anal Calcd for $C_{16}H_{13}NO\cdot 2H_2O$ (271.31): C, 70.83; H, 6.31; N, 5.16; (O), 17.69. Found: C, 70.26; H, 6.72; N, 5.05; (O), 17.97.

***N*-Benzyl-4-oxyisoquinolinium Betaine (1i).** *N*-Benzyl-4-oxyisoquinolinium betaine (**1i**) was prepared similar to **2i**, **2j**, and **3i** using *N*-benzyl-4-hydroxyisoquinolinium chloride. Yield: 72% dodecahydrate, yellow solid. Mp: 85−87 °C.

^1H NMR (DMSO-d_6): δ [ppm] = 8.16 (ddd, 1H, J_{meta} = 2.4 Hz, J_{ortho} = 6.8 Hz, J_{ortho} = 9.3 Hz, H-6/H-7), 7.90 (ddd, 1H, J_{meta} = 2.3 Hz, J_{ortho} = 6.8 Hz, J_{ortho} = 9.3 Hz, H-6/H-7), 7.63−7.48 (m, 4H, H-1, H-3, H-5, H-8), 7.40−7.37 (m, 5H, ar-H), 7.19 (s, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ [ppm] = 167.15 (C-4), 135.47 (ar-$C-CH_2$), 134.56, 129.53, 127.52, 126.93, 123.68, 119.83 (C-1, C-3, C-5, C-6, C-7, C-8), 129.3, 129.01 (C-9, C-10), 128.83, 128.19 (ar-CH-ortho, ar-CH-meta), 128.70 (ar-CH-para), 62.26 (CH_2).

IR (KBr): [cm^{-1}] = 3059 (ar C−H), 2958 (aliph C−H), 1568, 1502 (C=C, C=N), 750, 704 (ar C−H out of plane) and 1487, 1454, 1345, 1132, 882.

MS (FD): m/z (%) = 470 (4) [M_2^+], 236 (11) [MH^+], 235 (100) [M^+].

Anal Calcd for $C_{16}H_{13}NO\cdot 12\ H_2O$ (451.46): C, 42.57; H, 8.26; N, 3.10; (O), 46.07. Found: C, 43.05; H, 8.07; N, 3.08; (O), 45.80.

Polymerization Reactions. Homopolymerization Procedure. Poly[*N*-vinylbenzyl-3-hydroxypyridinium chloride] (2e). In a typical polymerization the monomer *N*-(vinylbenzyl)-3-hydroxypyridinium chloride (**2a**, 495 mg, 2 mmol), sodium chloride (580 mg, 1 mmol, 0.5 equiv), and the initiator potassium peroxodisulfate (11 mg, 40 μmol, 2 mol %) were dissolved in water (3 mL, 15 wt % solution based on the monomer), and the solution was degassed with nitrogen. The polymerization flask was sealed and put for 24 h into a bath preheated to 60−62 °C. The polymer was precipitated by dropping the solution into 2-propanol. After filtration, the polymer was dissolved in water and freeze-dried. Yield: 75%, colorless solid.

^1H NMR (D_2O): δ [ppm] = 8.24 (br s, 2H, H-2, H-6), 7.66 (br s, 2H, H-4, H-5), 6.98−6.24 (br m, 4H, ar-H), 5.38 (br s, 2H, N^+-CH_2), 1.23 (br s, 3H, H-14, CH_2-CH, CH_2-CH).

IR (KBr): [cm^{-1}] = 3387 (O−H), 3024 (ar C−H), 2926, 2853 (aliph C−H), 2729, 2613, 2506 (pyr O−H), 1603, 1584, 1509, 1491 (C=C, C=N), 807, 761 (ar C−H out of plane), and 1449, 1310, 1259, 1147, 1032, 872, 707, 684.

Poly[*N*-(2-hydroxy-1-methacryloyloxypropyl-3)-3-hydroxypyridinium chloride] (2f). Monomer: **2d**. Solvent: DMF. Initiator: AIBN. Precipitation polymerization: no further polymer could be isolated from the solvent. The obtained polymer was dissolved in a small amount of water, reprecipitated in 2-propanol, redissolved in water, and freeze-dried. Yield: 92% colorless solid.

^1H NMR (D_2O): δ [ppm] = 8.25 (br s, 2H, H-2, H-6), 7.81 (br s, 2H, H-4, H-5), 4.33−4.80 (br m, 5H, N^+-CH_2, $CH-OH$, CH_2-O), 1.92 (br s, 2H, CH_2-C), 1.16 (s, isot-CH_3), 0.99 (s, heterot-CH_3), 0.83 (s, syndiot-CH_3).

IR (KBr): [cm^{-1}] = 3332 (O−H), 3062 (ar C−H), 2958 (aliph C−H), 2750, 2628, 2500 (pyr O−H), 1728 (C=O), 1604, 1587, 1498 (C=C, C=N), 1161 (aliph C−OR) and 1456, 1319, 1274, 1123, 1031, 807, 685.

Poly[*N*-(2-hydroxy-1-methacryloyloxypropyl-3)-5-hydroxyisochinolinium chloride] (3f). Monomer: **3d**. Solvent: DMF. Initiator: AIBN. The polymer was precipitated in 2-propanol, filtered off, and dried to constant weight under reduced pressure. Yield: 92% light yellow solid.

^1H NMR (DMSO-d_6): δ [ppm] = 11.45 (br s, 1H, OH), 9.93 (br s, 1H, H-1), 8.63 (br s, 1H, H-3), 8.01 (br s, 1H, H-8), 7.45 (br s, 3H, H-4, H-6, H-7), 6.13 (br s, OH), 4.89−3.99 (br m, 5H, N^+-CH_2, $CH-OH$, CH_2-O), 2.07 (br s,2H, CH_2-C); 1.00 (br s, 3H, CH_3).

IR (KBr): [cm^{-1}] = 3391 (O−H), 3100 (ar C−H), 2730, 2615, 2520 (pyr O−H), 1728 (C=O), 1657, 1605, 1582, 1520 (C=C, C=N), 1185, 1155 (C−O) and 1475, 1449, 1400, 1297, 1249, 1119, 798, 759.

Poly[*N*-vinylbenzyl-4-hydroxyisochinolinium chloride] (1e). Monomer: **1a**. Solvent: water/acetonitrile (2:1). Initiator: potassium peroxodisulfate. Precipitation polymerization: further polymer was isolated from the solvent by precipitation in 2-propanol. After reprecipitation, the polymer was dried to constant weight under reduced pressure. Yield: 69% light yellow solid.

^1H NMR (DMSO-d_6): δ [ppm] = 7.62−7.20 (br m, 6H, H-1,H-3, H-5−8), 6.98−6.51 (br m, 4H, ar-H), 4.12 (br s, 2H, N^+-CH_2), 1.93 (br s, 3H, CH_2-CH, CH_2-CH).

IR (KBr): [cm^{-1}] = 3025 (ar C−H), 2950, 2840 (aliph C−H), 2502 (pyr O−H), 1692, 1602 (C=C, C=N), 766 (ar C−H out of plane), and 1458, 1138, 1127, 1108, 1023.

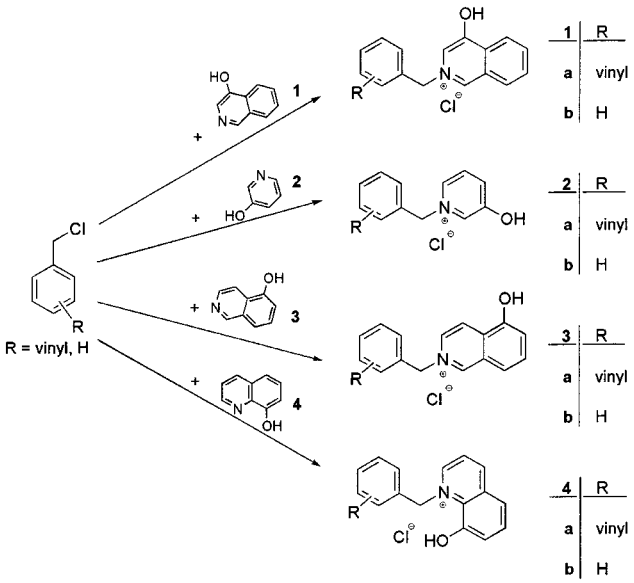
Copolymerization Procedure. Poly[*N*-vinylbenzyl-3-hydroxypyridinium chloride-*co*-styrene] (2g). In a typical polymerization, the monomer *N*-(vinylbenzyl)-3-hydroxypyridinium chloride (**2a**, 198 mg, 0.8 mmol), the comonomer styrene (417 mg, 4 mmol, 5 equiv), sodium chloride (24 mg, 0.4 mmol, 0.5 equiv), and the initiator AIBN (16 mg, 96 μmol, 2 mol %) were dissolved in acetonitrile (4 mL, 15 wt % solution based on the monomers) and the solution degassed with nitrogen. The polymerization flask was sealed and put for 24 h into a bath preheated to 60−62 °C. The polymer precipitated during the reaction. Dropping of the supernatant into 2-propanol yielded no further precipitate. The polymer was dissolved in a small amount of DMSO, reprecipitated in 2-propanol, filtered off, and dried to constant weight under reduced pressure. Yield: 69% colorless solid.

^1H NMR (DMSO-d_6): δ [ppm] = 8.87 (br s, 4H, H-2,H-4, H-5, H-6), 8.18−7,95 (br m, 4H, ar-H[salt]), 7.43−6.15 (br m, 25H, 5*(ar-H[styrene])), 5.79 (br s, 2H, N^+-CH_2), 1.54 (br s, 18H, CH_2-CH[salt], CH_2-CH[salt], 5*(CH_2-CH[styrene], CH_2-CH[styrene])).

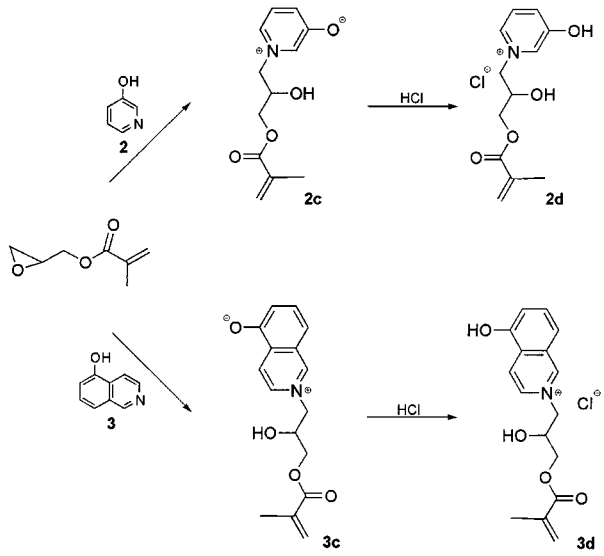
IR (KBr): [cm^{-1}] = 3385 (O−H), 3020 (ar C−H), 2921, 2849 (aliph C−H), 2725, 2603, 2500 (pyr-OH), 1601, 1583, 1509, 1492 (C=C, C=N), 807, 761, 702 (ar C−H out of plane), and 1451, 1311, 1259, 1147, 1030, 684.

Poly[*N*-(2-hydroxy-1-methacryloyloxypropyl-3)-3-hydroxypyridinium chloride-*co*-methyl methacrylate] (2h). Monomer: **2d**. Comonomer: MMA. Solvent: DMF. Initiator: AIBN. No precipitation of polymer during polymerization. The polymer obtained by precipitation in 2-propanol was dissolved in water and freeze-dried. Yield: 66% colorless solid.

Scheme 2



Scheme 3



^{1}H NMR (D_2O): δ [ppm] = 8.28 (br s, H-2, H-6), 7.81 (br s, H-4, H-5), 4.34−4.09 (br m, N^+-CH_2, $CH-OH$, CH_2-O), 3.55 (br s, $O-CH_3$), 1.87 (br s, CH_2-C[salt], CH_2-C[MMA]), 1.2−0.79 (br m, CH_3[salt], CH_3[MMA]).

IR (KBr): [cm^{-1}] = 3067 (ar C−H), 2997, 2951 (aliph C−H), 2750, 2629, 2500 (pyr O−H), 1727 (C=O), 1604, 1587, 1499 (C=C, C=N), 1191, 1157 (C−OR) and 1450, 1321, 1276, 1031, 807, 686.

Poly[*N*-(2-hydroxy-1-methacryloyloxypropyl-3)-5-hydroxyisochinolinium chloride-*co*-methyl methacrylate] (3 h). Monomer: **3d**. Comonomer: MMA. Solvent: DMF. Initiator: AIBN. Precipitation polymerization: no further polymer could be isolated from the solvent. Yield: 74% light yellow solid.

^{1}H NMR (DMSO-d_6): δ [ppm] = 11.45 (br s, hetar-O*H*), 9.93 (br s, H-1), 8.63 (br s, H-3), 8.01 (br s, H-8), 7.45 (br s, H-4, H-6, H-7), 6.13 (br s, CH−O*H*), 4.89−3.99 (br m, N^+-CH_2, $CH-OH$, CH_2-O),3.34 (br s, H_2O in DMSO-d_6 superimposed $O-CH_3$), 2.07 (br s, CH_2-C[salt], CH_2-C[MMA]), 1.00 (br s, CH_3[salt], CH_3[MMA]).

IR (KBr): [cm^{-1}] = 3348 (O−H), 3100 (ar C−H), 2952 (aliph C−H), 2731, 2616, 2521 (pyr O−H), 1727 (C=O), 1644, 1605, 1581, 1520 (C=C, C=N), 1185, 1155 (C−OR) and 1475, 1449, 1400, 1296, 798, 758.

Poly[*N*-vinylbenzyl-4-hydroxyisochinolinium chloride-*co*-styrene] (1 g). Monomer: **1a**. Comonomer: styrene. Solvent: water/acetonitrile (1:2). Initiator: AIBN. Precipitation polymerization: further polymer was isolated from the solvent. Yield: 75%, light yellow solid.

^{1}H NMR (DMSO-d_6): δ [ppm] = 7.65−7.20 (br m, H-1, H-3, H-5−8), 7.13−6.05 (br m, ar-H[salt and styrene]), 4.12 (br s, N^+-CH_2), 2.1−0.93 (br m, CH_2-CH, CH_2-CH[salt and styrene]).

IR (KBr): [cm^{-1}] = 3081, 3059, 3025 (ar C−H), 2922, 2848 (aliph C−H), 1694, 1601,1583, 1493 (C=C, C=N), 758, 698 (ar C−H out of plane) and 1452, 1370, 1306, 1291, 1028, 907.

Results and Discussion

4-Hydroxyisoquinoline (**1**) was synthesized according to the literature.[22,23] The quaternary *N*-styrene substituted salts **1a**−**4a** were prepared from 3-hydroxypyridine (**2**), 4- and 5-hydroxyisoquinoline (**1** and **3**), and 8-hydroxyquinoline (**4**) using vinylbenzyl chloride (Scheme 2).

The *N*-benzyl-substituted model compounds **1b**−**4b** (Scheme 2) were obtained following the same procedure using benzyl chloride instead of vinylbenzyl chloride.

Treatment of 3-hydroxypyridine (**2**) and 5-hydroxyisoquinoline (**3**) with glycidyl methacrylate yielded *N*-(2-hydroxy-1-methacryloyloxypropyl-3)-3-oxypyridinium betaine (**2c**) and *N*-(2-hydroxy-1-methacryloyloxypropyl-3)-5-oxyisoquinoline betaine (**3c**). They were converted into the quaternary salts **2d** and **3d** upon treatment with hydrochloric acid (Scheme 3).

Free radical homopolymerizations of the N-quaternary salts **1a**, **2a**, **2d**, and **3d** in polar solvents (water, water/acetonitrile or DMF) with potassium peroxodisulfate or AIBN as initiator and sodium chloride as a low molecular weight salt resulted in the ionic homopolymers **1e**, **2e**, **2f**, and **3f** (Scheme 4). The polyelectrolytes **2e** and **2f** consisting of the 3-hydroxypyridinium chloride derivatives were soluble in water, as expected.

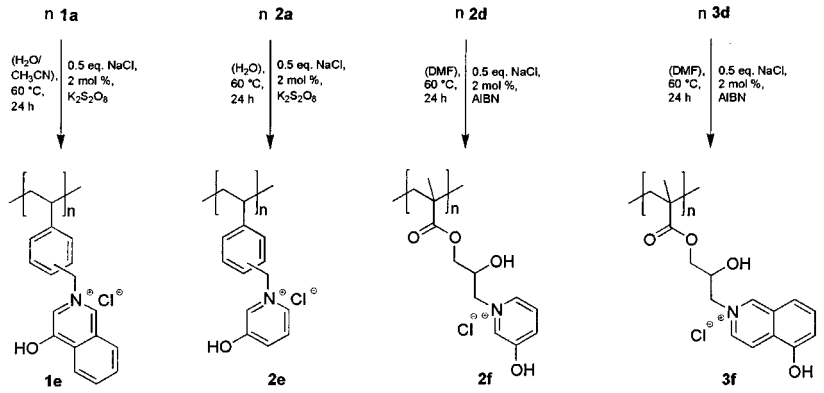
Copolymerization of the styrene based quaternary salts **1a** and **2a** with styrene and of the methacryloyl based salts **2d** and **3d** with MMA in a molar ratio of 1:5 respectively was realized as described above. From the obtained copolymers **1g**, **2g**, **2h**, and **3h** (Scheme 5) the *N*-methacryloyl based 3-hydroxypyridinium chloride/MMA copolymer **2h** showed good solubility in water.

To evaluate the exact copolymer compositions, well-defined integrated signals of the incorporated comonomers styrene (aromatic protons at 7.4−6.1 ppm) or MMA ($O-CH_3$ protons at 3.55 ppm) were compared to the area of the signals of the corresponding quaternized hydroxy *N*-heterocyle (benzylic protons at 8.18−7.95 ppm) in the ^{1}H NMR spectra. In correspondence to the initial molar ratio used, a proportion of incorporated styrene units to incorporated *N*-vinylbenzyl-3-hydroxypyridinium chloride units of 5:1 was found for copolymer **2g**. The nonconformance of the integration due to the extremely broadened proton signals permitted no exact evaluation of the other copolymer compositions.

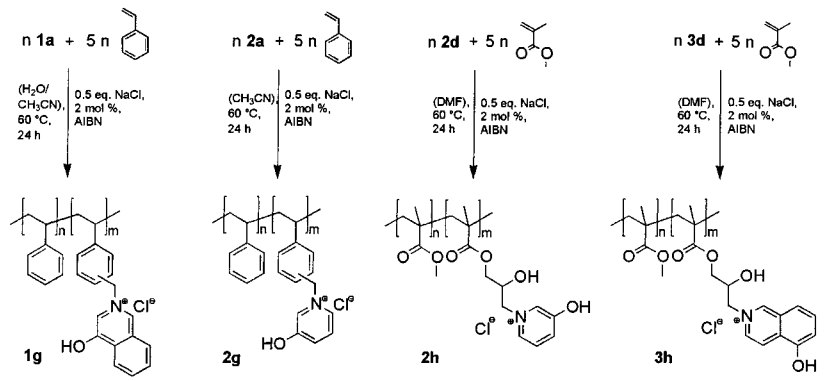
In most cases, the photosensitive dipolar betaine structure was generated in situ by adding triethylamine to a solution of the N-quaternary salts immediately before irradiation.

However, the low molecular weight betaines **1i**−**3i**, and **2j** (Scheme 6) were generated as model compounds by passing the corresponding ammonium salts through a column filled with basic anionic exchange resin (Amberlite IRA-410, OH^- form).

Scheme 4



Scheme 5



Scheme 6

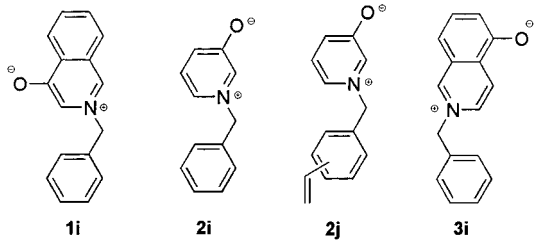
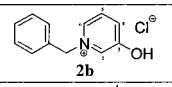
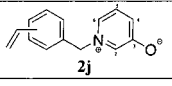


Table 1. ^{1}H NMR (200 MHz) Chemical Shifts and Coupling Constants of Heteroaromatic Protons in Oxypyridinium Derivatives 2b and 2j

Compound	H-2 δ [ppm] J [Hz]	H-4 δ [ppm] J [Hz]	H-5 δ [ppm] J [Hz]	H-6 δ [ppm] J [Hz]
 **2b**	8.83	8.11 $J_{2,4}$ = 2.2 $J_{4,5}$ = 8.5	7.95 $J_{5,6}$ = 5.9 $J_{4,5}$ = 8.5	8.72 $J_{5,6}$ = 5.9
 **2j**	7.60-7.35	6.86 $J_{2,4}$ = 2.4 $J_{4,5}$ = 8.8	7.24 $J_{5,6}$ = 5.4 $J_{4,5}$ = 8.8	7.60-7.35

^{1}H and ^{13}C NMR measurements documented a distinct change of electron density and distribution from the cationic hydroxyl N-quaternized structure to the highly dipolar betaine. In the 200 MHz ^{1}H NMR spectrum of *N*-benzyl-3-hydroxypyridinium chloride (**2b**) the signals of the protons in α-position to the heteroaromatic nitrogen appear at highest frequencies (Table 1). The corresponding 200 MHz ^{1}H NMR spectrum of *N*-vinylbenzyl-3-oxypyridinium betaine (**2j**) exhibits proton signals of the now overall uncharged dipolar *N*-heterocycle at comparably higher fields (Table 1).

The strongest displacement to higher magnetic field is found for the signals of the α-protons which are now within the range of the benzoaromatic proton signals. The dd signal of H-5 at 7.24 ppm shows a comparably risen ortho coupling of 8.8 Hz with H-4 (salt **2b**: 8.5 Hz) and a lowered ortho coupling of 5.4 Hz with H-6 (salt **2b**: 5.9 Hz).

An early comparative NMR spectroscopic study[24] on the structure of the two likewise uncharged substances 3-methoxypyridine and *N*-methyl-3-oxypyridinium betaine provided comparable changes in the ^{1}H NMR spectrum. The enhanced coupling of H-4 and H-5 in the betaine is explained by increased π-bonding order between C-4 and C-5. The particularly strong displacement of the α-proton signals to higher fields is attributed to a remarkably risen electron density at the α-carbons of the betaine. These conclusions are confirmed by PPP−MO calculations of total π-electron densities. While for 3-methoxypyridine electron density is reduced at the α-carbons, it is enhanced there for the betaine.[24]

By means of *N*-benzyl-4-oxyisochinolinium betaine (**1i**) in Figure 1, the similar distribution in the HOMO of the betaines is exemplified. The high orbital coefficients at C-2 and C-6 combined with the comparable high HOMO energy (E_{HOMO} = −4.98 eV, calculated by the DFT, pBP/DN* method implemented in PC Spartan Pro 1.07) and the opposite sign of the orbital coefficients explains their reactivity in thermal 1,3-dipolar cycloadditions with electron deficient olefins. In the corresponding LUMO (Figure 1) the size of the orbital coefficients at C-2 and C-6 remains nearly the same. The same sign of the orbital coefficients enables the betaines to form aziridines (e.g., Scheme 1) via photochemical induced disrotatory intramolecular ringclosure.

In the UV absorption spectra (10^{-4} M in dichloromethane), the highest wavelength absorption of the

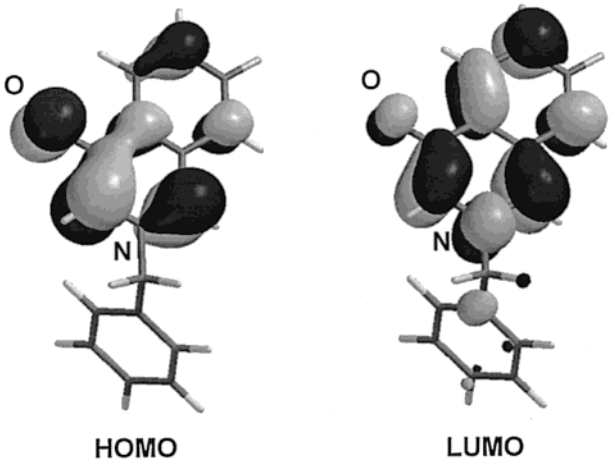


Figure 1. HOMO and LUMO of *N*-benzyl-4-oxyisochinolinium betaine (**1i**) calculated by the DFT, pBP/DN* method implemented in PC Spartan Pro 1.07.

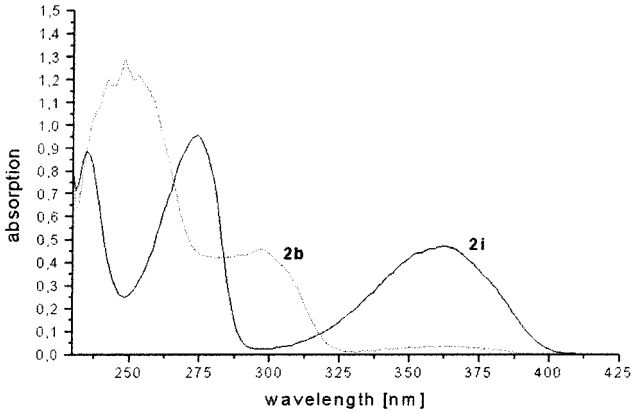


Figure 2. Absorption spectra of *N*-benzyl-3-hydroxypyridinium chloride (**2b**, dotted line) and its betaine (**2i**, solid line).

betaines is always found at remarkably higher wavelengths than the one of the corresponding salts, as shown in Figure 2 for *N*-benzyl-3-hydroxypyridinium chloride (**2b**, $\lambda_{max} = 305$ nm) and its betaine **2i** ($\lambda_{max} = 365$ nm).

The (co)polymers **1e**, **2e**, **2f**, **3f**, **1g**, **2g**, **2h**, and **3h** and model salts **1b**−**4b** were irradiated in the presence of triethylamine in dichloromethane solution (10^{-4} M) through a Pyrex filter using a xenon high-pressure lamp (600 W). The progress of the reaction was regularly monitored by recording UV absorption spectra. Figure 3 shows the absorption spectra recorded during irradiation of the copolymer poly[*N*-(2-hydroxy-1-methacryloyloxypropyl-3)-3-hydroxypyridinium chloride-*co*-methyl methacrylate] (**2h**) in the presence of TEA and Figure 4 those of the irradiation of *N*-benzyl-3-hydroxypyridinium chloride (**2b**).

The highest wavelength absorption degraded during irradiation of all model compounds and copolymers. Besides a further degrading absorption band at around 280 nm, which is probably assignable to a higher energetic transition of the betaine, the spectra of model compound **2b** shown in Figure 4 reveal the formation of a new absorption at around 300 nm corresponding to the development of the predicted carbonyl-aziridine type structure. Yet the copolymer spectra (see the exemplary spectra of copolymer **2h** in Figure 3) do not vary at lower wavelengths. As the bands are considerably broadened, it can be assumed that a simultaneous growth and

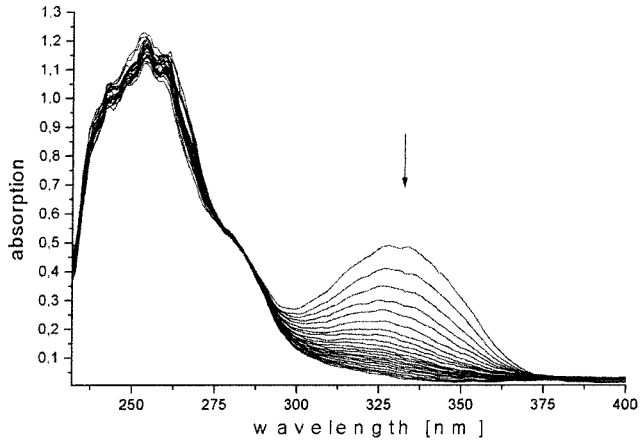


Figure 3. Absorption spectra recorded during the irradiation of copolymer **2h**, 10^{-4} M in dichloromethane + TEA.

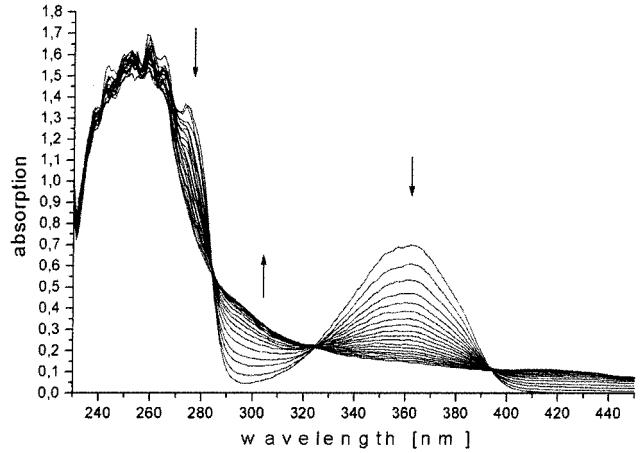


Figure 4. Absorption spectra recorded during the irradiation of salt **2b**, 10^{-4} M in dichloromethane + TEA.

Scheme 7

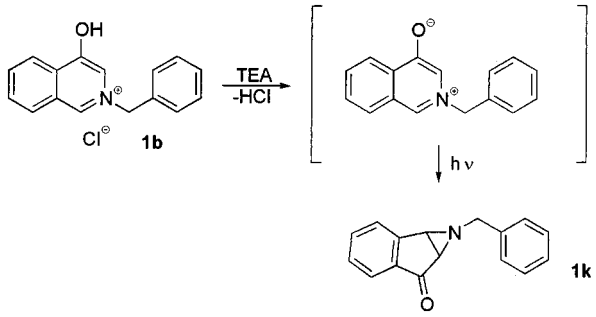
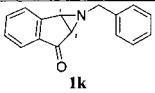


Table 2. Characteristic NMR and IR Data for Substance 1k

	^{1}H NMR (200 MHz) δ [ppm], J [Hz]	^{13}C NMR (50.3 MHz) δ [ppm]	IR [cm^{-1}]
 1k	3.19 (d, $J_{2,3}$ = 3.4, H-2) 2.90 (d, $J_{2,3}$ = 3.4, H-3) 3.70 (s, CH_2)	46.79 (C-2) 43.41 (C-3) 62.50 (CH_2)	1716 (C=O stretch vibration in α, β unsatured five membered ring

degradation of two bands in a comparably narrow wavelength range is not detectable.

In a preliminary quantitative experiment, *N*-benzyl-4-hydroxyisoquinolinium chloride (**1b**) was irradiated in the presence of triethylamine in dichloromethane. The formation of the expected aziridine 1-benzyl-1a,6a-

dihydroindeno[1,2-*b*]azirin-6(1*H*)-one (**1k**, Scheme 7), which was not isolated in pure form, could however be confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectra (Table 2).

Conclusion

N-Methacryloyl- and *N*-styrene-substituted hydroxypyridinium and hydroxyisoquinolinium salts readily form homo- or copolymers by a free radical polymerization. Polymer-bonded dipolar oxypyridinium and oxyisoquinolinium betaines are photosensitive, and for a model compound the expected aziridine structure was identified after irradiation. Thus, polymers with oxypyridinium or oxyisoquinolinium groups could potentially be suitable for the development of a new type of photosensitive material. In subsequent investigations, new substituted pyridinium and isoquinolinium betaines are to be prepared for further variation of absorption characteristics and physical properties.

References and Notes

(1) Theis, A.; Ritter, H. *Des. Monomers Polym.* **2001**, *4*, 177.
(2) Heinenberg, M.; Reihmann, M.; Ritter, H. *Des. Monomers Polym.* **2000**, *3*, 501.
(3) Heinenberg, M.; Ritter, H. *Macromol. Chem. Phys.* **1999**, *200*, 1792.
(4) Ritter, H.; Sperber, R.; Weisshuhn, C. M. *Macromol. Chem. Phys.* **1994**, *195*, 3823.
(5) Ritter, H.; Sperber, R. *Macromol. Rapid Commun.* **1995**, *16*, 407.
(6) Deutschmann, T.; Ritter, H. *Macromol. Rapid Commun.* **1995**, *17*, 723.
(7) Gotthardt, H.; Schenk, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 687.
(8) Böhme, F.; Menges, B.; Mittler, S.; Ritter, H.; Theis, A. *Chem. Mater.*, in press.
(9) Katritzky, A. R.; Rees, C. W.; Scriven In *Comprehensive Heterocyclic Chemistry II*, 2nd ed.; Pergamon Press: Oxford, England, 1996; Vol. 1a.
(10) Katritzky, A. R.; Rees, C. W. In *Comprehensive Heterocyclic Chemistry*, 1st ed.; Pergamon Press: Oxford, England, 1984; Vol. 2, Part 2A.
(11) Katritzky, A. R.; Dennis, N. In *New Trends in Heterocyclic Chemistry*; Elsevier: New York, 1979.
(12) Katritzky, A. R.; Boonyarakvanich, A.; Dennis, N. *J. Chem. Soc., Perkin Trans. 1* **1980**, 343.
(13) Katritzky, A. R.; Rahimi-Rastgoo, S.; Sabongi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 362.
(14) Katritzky, A. R.; Banerji, J.; Dennis, N. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2528.
(15) Katritzky, A. R.; Cutler, A. T.; Dennis, N. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1176.
(16) Katritzky, A. R.; Dennis, N.; Dowlatshahi, H. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 331.
(17) Dennis, N.; Katrizky, A. R.; Wilde, H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2339.
(18) Dennis, N.; Katritzky, A. R.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2054.
(19) Garling, D. L.; Cromwell, N. H. *J. Org. Chem.* **1973**, *38*, 654.
(20) Dennis, N.; Katritzky, A. R.; Parton, S. K. *Chem. Pharm. Bull.* **1975**, *23*, 2899.
(21) Hansen, P. E.; Undheim, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 305.
(22) Constable, K. P.; Carroll, F. I. *Heterocycl. Commun.* **1996**, *2* (1), 13.
(23) Bacon, R. G. R.; Rennison, S. C. *J. Chem. Soc. C* **1969**, 312.
(24) Vögeli, U.; v. Philipsborn, W. *Org. Magn. Reson.* **1973**, *5*, 551.
(25) Pham, V. C.; Charlton, J. L. *J. Org. Chem.* **1995**, *60*, 8051.
(26) Shapiro, S. L.; Weinberg, K.; Freedman, L. *J. Am. Chem. Soc.* **1959**, *81*, 5140.

MA011750B