Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 4617–4619

TETRAHEDRON LETTERS

Synthesis of ligand monomers derived from 4,5-diazafluoren-9-one☆

Guangchang Zhou and Issifu I. Harruna*

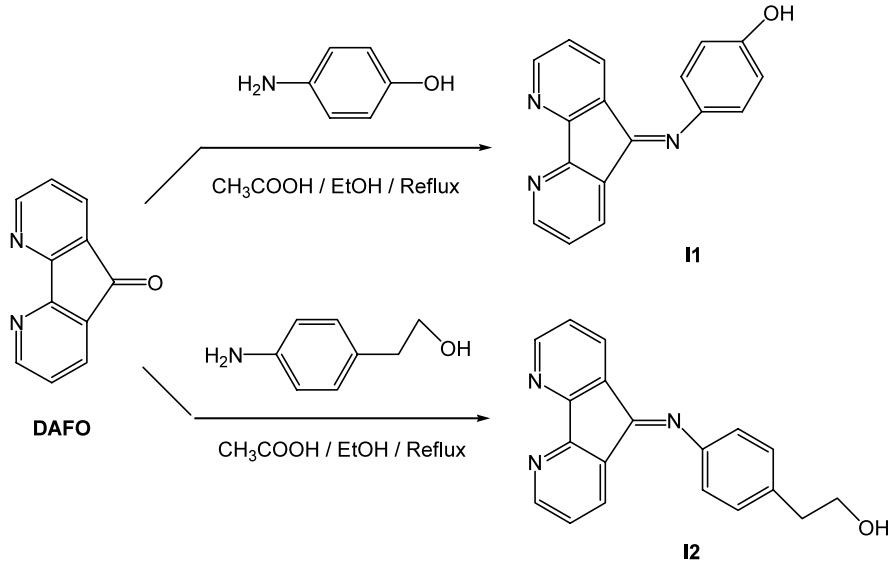
Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive SW, Atlanta, GA 30314, USA

Received 27 February 2003; revised 19 March 2003; accepted 24 March 2003

Abstract—This report describes a convenient two-step synthesis of free radical polymerizable ligand monomers starting from 4,5-diazafluoren-9-one.

In recent years, the synthesis of metal-containing polymers has attracted considerable attention due to their numerous applications in the fields of catalysis, conducting and photoresponsive materials, as well as in supramolecular chemistry.[1] Due to their high binding affinity for transition metal ions, 2,2′-bipyridine-, 1,10-phenanthroline-type ligands are useful for introducing metal binding sites into polymers.[2] Therefore, some bipyridine-containing monomers were synthesized and used for synthesis of metal-containing polymers.[2–5] Here we report on the synthesis of novel bipyridine-based polymerizable ligand momomers.

The commercially available ligand compound, 4,5-diazafluoren-9-one, in the presence of catalytic acetic acid condensed with 4-aminophenol and 4-aminophenylethyl alcohol to produce two intermediate **I1** and **I2**, respectively (Scheme 1). The two intermediate **I1** and **I2** were further reacted with methacryloyl chloride respectively with catalytic triethylamine to give



Scheme 1.

☆ Supplementary data associated with this article can be found at doi:10.1016/S0040-4039(03)00747-0

* Corresponding author. Tel.: +1-404-880-6883; fax: +1-404-880-6890; e-mail: iharruna@cau.edu

0040-4039/03/$ - see front matter
doi:10.1016/S0040-4039(03)00747-0

two polymerizable ligand monomers **M1** and **M2**, respectively (Scheme 2). The two ligand monomers were further purified by recrystallization from ethyl alcohol.

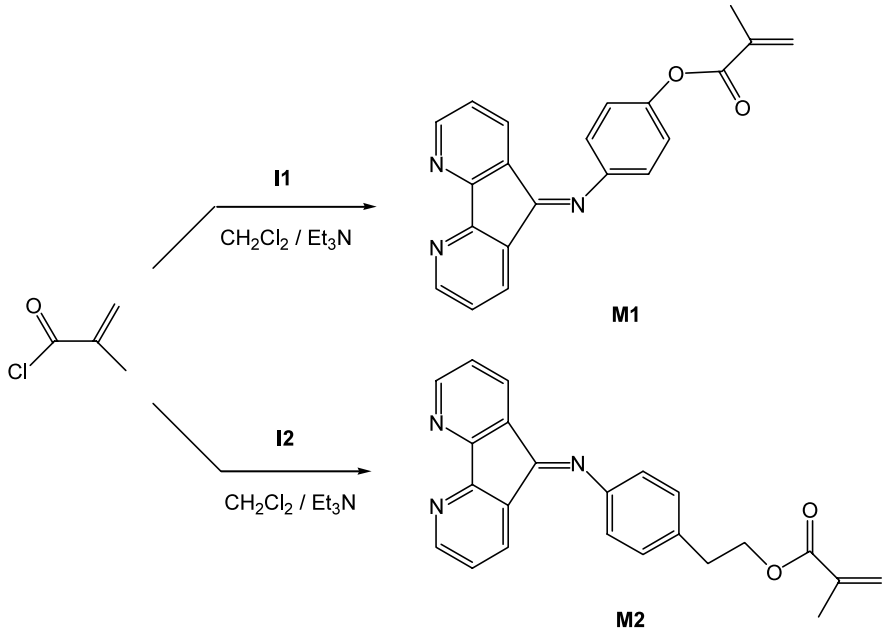
In addition, 4,5-diazafluoren-9-one (DAFO) reacted with vinylmagnesium bromide which further hydrolyzed to produce 9-hydroxyl-9-vinyl-4,5-diazafluorene (**M3**) (Scheme 3). The crude ligand monomer **M3** was recrystallized from chloroform to give the pure monomer **M3**. The monomer **M3** was further converted into the monomer **M4** by methacrylation with methacryloyl chloride with catalytic triethylamine (Scheme 3). All three methacrylate-typed ligand monomers, **M1**, **M2** and **M4** were co-polymerized with styrene to give three bipyridine-containing co-polymers. A detailed study of the homo- and co-polymerization of the three monomers is in progress.

Experimental

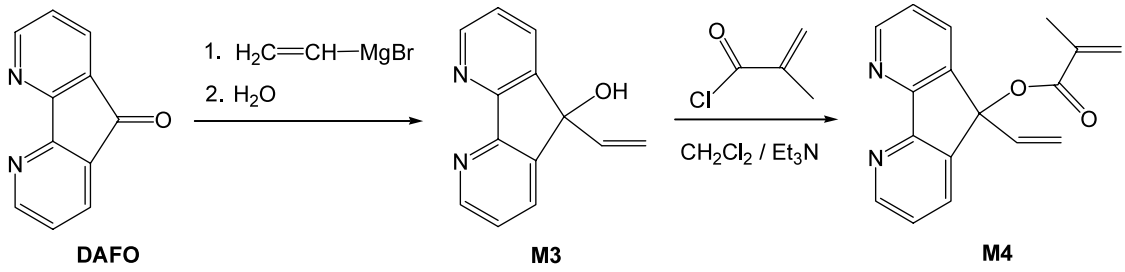
NMR spectra were acquired on a Bruker ARX400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C. High-resolution mass spectrometry (HRMS) was performed on a VG Instruments 70SE using electron-impact (EI) ionization. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration.

Synthesis of the intermediate I1: a mixture of DAFO (450 mg, 2.470 mmol), glacial acetic acid (0.20 ml, 3.494 mmol), ethanol (30 ml) and 4-aminophenol (270 mg, 2.474 mmol) was heated at 80°C for 18 h. The resulting reaction mixture was cooled to −20°C, then filtered and washed with cold ethanol three times, and finally dried under vacuum at 40°C to give 529 mg of the intermediate **I1** (78%). Mp 317.5–318°C. ^{1}H NMR (DMSO-d_6): δ 9.56 (b, 1H, OH), 8.79 (d, 1H), 8.66 (d, 1H), 8.25 (d, 1H), 7.52 (q, 1H), 7.25 (q, 1H), 7.11 (d, 1H), 6.95 (m, 4H). ^{13}C NMR (DMSO-d_6): 160.6, 159.1, 157.2, 155.2, 152.8, 152.2, 142.0, 132.9, 132.4, 130.2, 125.8, 124.6, 123.7, 120.1, 115.9. HRMS (EI): calcd for $C_{17}H_{11}N_3O$ $m/z=273.0902$, found $m/z=273.0897$.

Synthesis of the intermediate I2: a mixture of DAFO (1115 mg, 6.120 mmol), glacial acetic acid (0.50 ml, 8.734 mmol), ethanol (45 ml) and 4-aminophenethyl alcohol (870 mg, 6.342 mmol) was heated at 80°C for 17 h. The resulting reaction mixture was cooled to −20°C, then filtered and washed with cold ethanol three times, and finally dried under vacuum at 40°C to give 1229 mg of the intermediate **I2** (67%). Mp 235–236°C.



Scheme 2.



Scheme 3.

^{1}H NMR (DMSO-d_6): δ 8.83 (d, 1H), 8.68 (d, 1H), 8.29 (d, 1H), 7.56 (q, 1H), 7.36 (d, 2H), 7. 23 (q, 1H), 7.02 (d, 2H), 6.91 (d, 1H), 4.78 (t, 1H, OH), 3.74 (t, 2H), 2.86 (t, 2H). ^{13}C NMR (DMSO-d_6): 160.8, 159.2, 157.5, 153.0, 152.4, 148.4, 136.3, 133.1, 132.1, 130.4, 129.8, 125.8, 124.6, 123.6, 118.0, 62.1, 38.5. HRMS (EI): calcd for $C_{19}H_{15}N_3O$ $m/z=301.1215$, found $m/z=301.1205$.

Synthesis of the monomer M1: methacryloyl chloride (150 mg, 1.435 mmol) and 0.40 ml (2.870 mmol) of triethylamine was mixed with 5 ml of THF to give a solution. The solution was added dropwise into a dispersion solution of the intermediate **I1** (200 mg, 0.733 mmol) in 70 ml CH_2Cl_2. After addition, the reaction mixture was stirred at room temperature for 3 h. The resulting reaction solution was washed with 1% NaOH solution and distilled water until neutral, was then dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum to give 248 mg of crude monomer **M1** (99%). The crude monomer was further recrystallized from ethyl alcohol to give pure monomer **M1**. Mp 187–188°C. ^{1}H NMR ($CDCl_3$): δ 8.80 (d, 1H), 8.66 (d, 1H), 8.23 (d, 1H), 7.39 (q, 1H), 7.22 (d, 2H), 7.03 (m, 4H), 6.36 (s, 1H, vinyl), 5.80 (s, 1H, vinyl), 2.10 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 165.8, 161.5, 159.9, 158.8, 153.3, 152.7, 148.2, 148.10, 135.7, 133.7, 132.3, 130.5, 127.3, 126.0, 124.1, 123.3, 122.6, 119.1, 18.3. HRMS (EI): calcd for $C_{21}H_{15}N_3O_2$ $m/z=341.1164$, found $m/z=341.1154$.

Synthesis of the monomer M2: methacryloyl chloride (85 mg, 0.813 mmol) and 0.20 ml (1.435 mmol) of triethylamine was mixed with 5 ml of THF to give a solution. The solution was added dropwise into a solution of the intermediate **I2** (200 mg, 0.664 mmol) in 50 ml CH_2Cl_2. After addition, the reaction mixture was stirred at room temperature for 2.5 h. The resulting solution was washed in turn with 1% NaOH solution and distilled water until neutral, was then dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum to give 236 mg of crude monomer **M2** (96%). The crude monomer was further recrystallized from ethyl alcohol to give pure monomer **M2**. Mp 146–145°C. ^{1}H NMR ($CDCl_3$): δ 8.81 (d, 1H), 8.66 (d, 1H), 8.24 (d, 1H), 7.39 (q, 1H), 7.31 (d, 2H), 6.98 (q, 1H), 6.94 (d, 2H), 6.88 (d, 1H), 6.11 (s, 1H), 5.57 (s, 1H), 4.46 (t, 2H), 3.05 (t, 2H), 1.95 (s, 3H). ^{13}C NMR ($CDCl_3$): 167.2, 161.4, 159.8, 158.4, 153.2, 152.5, 149.3, 136.2, 134.7, 133.7, 132.4, 130.4, 129.9, 126.1, 125.4, 124.1, 123.1, 118.5, 65.2, 34.6, 18.3. HRMS (EI): calcd for $C_{23}H_{19}N_3O_2$ $m/z=369.1477$, found $m/z=369.1468$.

Synthesis of the monomer M3: vinylmagnesium bromide (6.0 ml, 1.0 M in THF) was added dropwise to a solution of 0.910 g of DAFO in 100 ml THF. The mixture was heated under reflux for 2.5 h and hydrolyzed by addition of saturated ammonium chloride solution (200 ml). Dichloromethane was then added. The organic phase was separated, dried over anhydrous magnesium sulfate overnight. The solvent was removed under reduced pressure to give 1.050 g of crude monomer **M3**. The monomer **M3** was recrystallized from chloroform; yield 0.535 g (51%). Mp 208–209°C. ^{1}H NMR (DMSO-d_6): δ 8.61 (d, 2H), 7.84 (d, 2H), 7.39 (q, 2H), 6.20 (s, 1H, OH), 5.97 (q, 1H), 5.37 (d, 1H), 5.17 (d, 1H); ^{13}C NMR (DMSO-d_6): δ 156.9, 150.4, 144.0, 139.3, 132.4, 123.9, 113.8, 77.7. HRMS (EI): calcd for $C_{13}H_{10}N_2O$ $m/z=210.0793$, found $m/z=210.0790$.

Synthesis of the monomer M4: methacryloyl chloride (1.943 g, 18.683 mmol) and 2.280 g (22.570 mmol) of triethylamine was mixed with 20 ml of dry CH_2Cl_2 to give a solution. The solution was added dropwise to a solution of the monomer **M3** (1.250 g, 5.952 mmol) in 150 ml of CH_2Cl_2. After addition, the reaction mixture was stirred at room temperature for 72 h. The resulting reaction solution was washed in turn with 1% NaOH solution and distilled water until neutral, was then dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum to give crude monomer **M4**. The crude monomer was further recrystallized from ethyl alcohol to give pure brown monomer **M4** (32%). Mp 143.5–144°C. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 2H), 7.86 (d, 2H), 7.28 (q, 2H), 6.11 (s, 1H), 6.07 (t, 1H), 5.59 (s, 1H), 5.42 (d, 1H), 5.26 (d, 1H), 1.88 (s, 3H). ^{13}C NMR ($CDCl_3$): 165.1, 157.9, 151.2, 139.7, 136.1, 135.4, 132.2, 126.3, 123.5, 115.5, 83.7, 18.2. HRMS (EI): calcd for $C_{17}H_{14}N_2O_2$ $m/z=278.1055$, found $m/z=278.1055$.

Supplementary material

^{1}H and ^{13}C NMR spectra, GC–MS and HRMS of all compounds are provided in the online version of this paper.

Acknowledgements

This study was supported by Office of Naval Research (ONR Grant No. N00014-01-1-1042).

References

1. (a) Sauvage, J. P. *Transition Metals in Supramolecular Chemistry*, *Perspectives in Supramolecular Chemistry Series*; Wiley: New York, 1999; Vol. VI; (b) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641.
2. Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892.
3. Schultze, X.; Serin, J.; Adronov, A.; Frechet, J. M. J. *Chem. Commun.* **2001**, 1160.
4. Serin, J.; Schultze, X.; Adronov, A.; Frechet, J. M. J. *Macromolecules* **2002**, *35*, 5396.
5. Antonietti, M.; Lohmann, S.; Eisenbach, C. D.; Schubert, U. S. *Macromol. Rapid Commun.* **1995**, *16*, 283.