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A new diamido-amine ligand based on three-carbon atom "arms": synthesis, structures and polymerisation capability of zirconium derivatives of MeN(CH₂CH₂CH₂NSiMe₃)₂

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Electronic supporting information:

Selected characterising data

[MeN(CH₂CH₂CH₂N(H)SiMe₃)₂]₂ (1-H₂)

¹H NMR data (C₆D₆, 300.1 MHz, 293 K): 2.76 (4H, dt, N(H)C<u>H</u>₂, ³*J* = 6.8, 7.9 Hz), 2.30 (4 H, t, NCH₂, ³*J* = 6.8 Hz), 2.12 (3 H, s, NMe), 1.50 (4 H, quin, NCH₂C<u>H</u>₂, ³*J* = 6.8 Hz), 0.42 (2 H, br. S, NH), 0.12 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (C₆D₆, 125.7 MHz, 293 K): 55.7 (NCH₂), 42.3 (NMe), 40.3 (NCH₂), 32.2 (NCH₂CH₂), -0.1 (SiMe₃) ppm. IR data (NaCl plates, film): 3328 (w, br.) (v(NH)), 2950 (s), 2898 (s), 2840 (s), 2790 (s), 1464 (m), 1436 (w), 1398 (m), 1356 (w), 1292 (w), 1248 (s), 1174 (w), 1142 (m), 1130 (w), 1108 (s), 1056 (w), 954 (w), 876 (s), 838 (s), 744 (m), 680 (m) cm⁻¹. HR EI-MS for [MeN(CH₂CH₂CH₂N(H)SiMe₃)₂]⁺, found (calc. for C₁₃H₃₅N₃Si₂): *m/z* = 289.2379 (289.2370).

[MeN(CH₂CH₂CH₂N(Li)SiMe₃)₂]₂ (1-Li₂)

¹H NMR data (C₆D₆, 500.0 MHz, 293 K): 3.43 (2 H, m, NC<u>H</u>₂CH₂CH₂CH₂N), 3.19 (2 H, m, NC<u>H</u>₂CH₂CH₂N), 2.10 (2 H, m, NCH₂CH₂C<u>H</u>₂N), 1.83 (2 H, m, NCH₂CH₂C<u>H</u>₂N), 1.76 (3 H, s, NMe), 1.38 (4 H, br. S, NCH₂C<u>H</u>₂CH₂N), 0.26 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (C₆D₆, 125.7 MHz, 293 K): 59.7 (NCH₂CH₂CH₂N), 49.3 (N<u>C</u>H₂CH₂CH₂CH₂N), 43.8 (NMe), 33.3 (NCH₂<u>C</u>H₂CH₂N), 3.0 (SiMe₃) ppm. ⁷Li NMR data (C₆D₆, 194.6 MHz, 293 K): 2.28 (br. s), 1.66 (br. s) ppm. IR data (KBr pellet): 2802 (s), 2706 (m), 2674 (m), 2602 (w), 1584 (m), 1460 (s), 1432 (m), 1384 (m), 1364 (m), 1352 (m), 1308 (w), 1244 (s), 1182 (m), B412381F ESI - page 1

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1114 (s), 1084 (s), 1058 (s), 1036 (m), 976 (m), 958 (w), 824 (m), 736 (m), 710 (w), 668 (m), 658 (m), 606 (w), 530 (m), 480 (w), 456 (w), 440 (w), 416 (w) cm⁻¹. HR EI-MS for $[Li_2{MeN(CH_2CH_2CH_2NSiMe_3)_2}]^+$, found (calc. for $C_{13}H_{35}Li_2N_3Si_2$): m/z = 301.2525 (301.2533). Anal. Found (calc. for $C_{26}H_{66}Li_4N_6Si_4$): C 51.8 (51.8), H 11.1 (11.0), N 13.9 (13.9) %.

$[Zr(N_2N^{C3})Cl_2]$ (2)

¹H NMR data (toluene-d₈, 300.1 MHz, 223 K): 3.73 (2 H, m, NCH₂CH₂CH₂N), 3.00 (2 H, m,

NCH₂CH₂CH₂N), 2.82 (2 H, m, NCH₂CH₂CH₂N), 2.04 (3 H, s, NMe), 1.58 (1 H, d, NCH₂CH₂CH₂N, ${}^{2}J$ = 13.0 Hz), 1.22 (3 H, m, NCH₂CH₂CH₂N), 0.83 (3 H, m, NCH₂CH₂CH₂N), 0.40 (9 H, s, SiMe₃), 0.30 (9 H, s, SiMe₃) ppm. ${}^{13}C{}^{1}H$ NMR data (toluene-d₈, 125.7 MHz, 223 K): 62.2 (NCH₂CH₂CH₂N), 58.6 (NCH₂CH₂CH₂N), 47.4 (NCH₂CH₂CH₂N), 46.7 (NMe), 42.9 (NCH₂CH₂CH₂N), 27.3 (NCH₂CH₂CH₂N), 27.2 (NCH₂CH₂CH₂N), 0.1 (SiMe₃), -0.4 (SiMe₃) ppm. IR data (NaCl plates, Nujol): 2361 (m), 1251 (m), 1169 (w), 1146 (m), 1127 (m), 1052 (m), 1002 (m), 959 (w), 919 (w), 878 (w), 842 (s), 787 (m), 680 (w) cm⁻¹. HR EI-MS for [Zr(N₂N^{C3,Me})Cl₂]⁺, found (calc. for C₁₃H₃₃Cl₂N₃Si₂Zr): *m/z* = 447.0629 (447.0637). Anal. Found (calc. for C₁₃H₃₃Cl₂N₃Si₂Zr): C 34.7 (34.7), H 7.6 (7.4), N 9.3 (9.3) %.

$[Zr(N_2N^{C3})(CH_2Ph)_2]$ (3)

¹H NMR data (toluene-d₈, 500.0 MHz, 213 K): 7.39 (2 H, m, *m*-C₆H₅ (b)), 7.27 (4 H, overlapping m, *m*-C₆H₅ (a), *o*-C₆H₅ (b)), 7.05 (1 H, m, *p*-C₆H₅ (b)), 6.93 (1 H, m, *p*-C₆H₅ (a)), 6.46 (2 H, d, *o*-C₆H₅ (a), ³*J* = 5.9 Hz), 3.63 (2 H, d, NCH₂CH₂CH₂N, ²*J* = 12.7 Hz), 3.19 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 16.1 Hz), 2.87 (2 H, m, NCH₂CH₂CH₂N), 2.73 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 14.0 Hz), 2.42 (4 H, m, CH₂C₆H₅), 1.83 (3 H, s, NMe), 1.33 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 10.5 Hz), 1.17 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 12.0 Hz), 1.07 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 12.0 Hz), 0.93 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 10.8 Hz), 0.84 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 13.9 Hz), 0.71 (1 H, d, NCH₂CH₂CH₂N, ²*J* = 11.2 Hz), 0.34 (9 H, s, SiMe₃), 0.23 (9 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (toluene-d₈, 125.7 MHz, 213 K): 151.7 (*ipso*-C₆H₅), 150.9 (*ipso*-C₆H₅), B412381F ESI - page 2

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128.4 (m-C₆H₅ (b)), 127.5 (o-C₆H₅ (b)), 126.3 (m-C₆H₅ (a)), 125.7 (o-C₆H₅ (a)), 121.0 (p-C₆H₅ (a)), 119.6 (p-C₆H₅ (b)), 69.9 (NCH₂CH₂CH₂N), 63.6 (NCH₂CH₂CH₂CH₂N), 61.7 (NCH₂CH₂CH₂N), 57.8 (NCH₂CH₂CH₂N), 45.5 (NMe), 44.1 (NCH₂CH₂CH₂N), 40.1 (NCH₂CH₂CH₂N), 28.1 (<u>C</u>H₂C₆H₅), 27.9 (<u>C</u>H₂C₆H₅), 1.8 (SiMe₃), 0.3 (SiMe₃) ppm. IR data: (KBr pellet): 2854 (s), 2812 (s), 2740 (w), 2664 (w), 1922 (w), 1870 (w), 1592 (s), 1488 (s), 1438 (m), 1396 (w), 1242 (s), 1208 (s), 1174 (s), 1004 (s), 950 (s), 918 (m), 794 (m), 744 (m), 694 (m), 680 (m), 626 (w), 610 (w), 530 (m), 510 (w), 464 (w), 446 (w), 424 (w), 408 (m) cm⁻¹. EI-MS: m/z = 468 (50 %) [M - CH₂Ph]⁺, 413 (15 %) [M - 2 SiMe₃]⁺, 377 (60 %) [M - 2 CH₂Ph]⁺. Anal. Found (calc. for C₂₇H₄₇N₃Si₂Zr): C 57.3 (57.8), H 8.0 (8.4), N 7.7 (7.5) %.

$[Zr(N_2N^{C2,Me})Cl_2]_2$ (4)

¹H NMR data (benzene-d₆, 300 MHz, 293 K): 3.17 (4 H, m, Me₃SiNC<u>H₂</u>CH₂N), 3.03 (4 H, m, Me₃SiNC<u>H₂</u>CH₂N), 2.36 (4H, m, Me₃SiNCH₂C<u>H₂N), 2.02 (6H, s, NMe), 1.96 (4H, m, Me₃SiNCH₂C<u>H₂N), 0.43 (36H, s, SiMe₃) ppm. ¹³C {¹H} NMR data (benzene-d₆, 125.7 MHz, 293 K): 59.8 (Me₃SiNCH₂<u>C</u>H₂N), 48.8 (Me₃SiN<u>C</u>H₂ CH₂N), 43.8 (NMe), -0.1 (SiMe₃) ppm. IR data (KBr plates, Nujol): 4335 (w), 3932 (w), 3903 (w), 3882 (w), 3871 (w), 3853 (w), 3839 (w), 3821 (w), 3801 (w), 3780 (w), 3750 (w), 3735 (w), 3711 (w), 3690 (w), 3675 (w), 3649 (w), 3629 (w), 3618 (w), 3587 (w), 3567 (w), 3546 (w), 3525 (w), 3503 (w), 3278 (w), 3131 (w), 1943 (w), 1923 (w), 1869 (w), 1845 (w), 1830 (w), 1793 (w), 1772 (w), 1749 (w), 1734 (w), 1717 (w), 1699 (w), 1684 (w), 1670 (w), 1654 (w), 1636 (w), 1624 (w), 1577 (w), 1559 (w), 1541 (w), 1522 (w), 1508 (w), 1489 (w), 1417 (w), 1398 (w), 1296 (w), 1182 (w), 1125 (w), 1052 (w), 989 (w), 944 (w), 922 (w), 911 (w), 746 (m), 677 (m), 626 (w), 598 (m), 566 (w), 553 (w), 526 (w), 458 (w), 444 (m), 420 (w) cm⁻¹. HR EI-MS for [Zr(N₂N^{C2,Me})Cl₂]⁺, found (calc. for C₁₁H₂₉Cl₂N₃Si₂Zr): *m/z* = 419.0332 (419.0324). Anal. Found (calc. for C₁₁H₂₉Cl₂N₃Si₂Zr): C 31.4 (31.3), H 7.0 (6.9), N 9.9 (9.9) %.</u></u>

 $[Zr(N_2N^{C2,Me})(CH_2Ph)_2]$ (5)

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¹H NMR data (benzene-d₆, 300.1 MHz, 293K): 7.08 (8 H, overlapping m, *o*-C₆H₅, *m*-C₆H₅), 6.76 (2 H, br t, *p*-C₆H₅), 3.24 (2 H, dt, Me₃SiNC<u>H₂</u>CH₂N, J = 4.1, 12.3 Hz), 2.89 (2 H, dd, Me₃SiNC<u>H₂</u>CH₂N, J = 5.3, 13.0 Hz), 2.74 (2 H, s, C<u>H₂</u>C₆H₅), 2.58 (2 H, s, C<u>H₂</u>C₆H₅), 2.00 (2 H, dt, Me₃SiNCH₂C<u>H₂N</u>, J = 6.16, 11.60 Hz), 1.74 (2 H, dd, Me₃SiNCH₂C<u>H₂N</u>, J = 3.48, 11.2 Hz), 1.29 (3 H, s, NMe), 0.46 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (benzene-d₆, 125.7 MHz, 293 K): 146.9 (*ipso*-C₆H₅), 145.1 (*ipso*-C₆H₅), 129.9, 128.3, 128.2, 127.7 (*o*-C₆H₅ and *p*-C₆H₅), 121.2 (*p*-C₆H₅), 121.1 (*p*-C₆H₅), 67.0 (CH₂C₆H₅), 64.8 (CH₂C₆H₅), 63.9 (Me₃SiNCH₂CH₂N), 50.2 (Me₃SiNCH₂CH₂N), 36.7 (NMe), 1.4 (SiMe₃) ppm. IR data (NaCl plates, Nujol): 1592 (m), 1301 (w), 1246 (m), 1200 (w), 1074 (m), 1027 (m), 937 (m), 912 (m), 835 (s), 746 (m), 694 (m), 581 (m) cm⁻¹. Anal. Found (calc. for C₂₅H₄₃N₃Si₂Zr): C 54.5 (56.3), H 8.0 (8.1), N 7.9 (7.8) %. Repeated crystallisations and analyses did not improve the low %C analysis for this crystalline compound, which is tentatively attributed to zirconium carbide formation.

$[Zr(N_2N^{C3})Me_2]$ (6)

¹H NMR data (toluene-d₈, 300.1 MHz, 203 K): 3.90 (1 H, m, NCH₂CH₂CH₂N), 3.51 (1 H, t, NCH₂CH₂CH₂N, ${}^{3}J$ = 13.2 Hz), 3.00 (3 H, m, NCH₂CH₂CH₂N), 2.33 (1 H, m, NCH₂CH₂CH₂N), 1.75 (3 H, br s, NMe), 1.49 (1 H, br d, NCH₂CH₂CH₂N, ${}^{2}J$ = 12.4 Hz), 1.28 (1 H, m, NCH₂CH₂CH₂N), 1.13 (1 H, br d, NCH₂CH₂CH₂N, ${}^{2}J$ = 12.4 Hz), 0.88 (2 H, m, NCH₂CH₂CH₂N), 0.61 (3 H, s, ZrMe), 0.54 (3 H, s, ZrMe), 0.43 (9 H, s, SiMe₃), 0.29 (9 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (toluene-d₈, 125.7 MHz, 203 K): 62.3 (NCH₂CH₂CH₂N), 57.8 (NCH₂CH₂CH₂N), 45.2 (overlapping NCH₂CH₂CH₂N and NMe), 39.2 (NCH₂CH₂CH₂N), 37.7 (ZrMe), 32.8 (ZrMe), 28.6 (NCH₂CH₂CH₂N), 28.5 (NCH₂CH₂CH₂N), 0.5 (SiMe₃), 0.4 (SiMe₃) ppm. IR data (NaCl plates, Nujol): 1244 (s), 1175 (w), 1135 (m), 1082 (m), 1049 (m), 966 (m), 952 (s), 918 (m), 876 (s), 834 (s), 785 (s), 744 (m), 679 (m), 624 (w) cm⁻¹. Anal. Found (calc. for C₁₅H₃₉N₃Si₂Zr): C 42.7 (44.1), H 9.3 (9.6), N 10.6 (10.3) %. This compound is an oil and cannot be further purified by crystallisation or sublimation.

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[Zr(N₂N^{C3})Me][B(C₆F₅)₄] (7) (NMR tube scale synthesis only)

¹H NMR data (C₆D₅Br, 300.1 MHz, 293 K): 3.57 (2 H, m, NCH₂CH₂CH₂N), 3.39 (2 H, m,

NCH₂CH₂CH₂N), 2.33 (2 H, m, NCH₂CH₂CH₂N), 2.03 (2 H, m, NCH₂CH₂CH₂N), 1.95 (3 H, s, NMe), 1.26 (4 H, m, NCH₂CH₂CH₂N), 0.31 (3 H, s, ZrMe), -0.07 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR data (C₆D₅Br, 125.7 MHz, 293 K): 60.0 (NCH₂CH₂CH₂N), 51.1 (ZrMe), 45.0 (NMe), 42.1 (NCH₂CH₂CH₂N), 28.1 (NCH₂CH₂CH₂N), 0.7 (SiMe₃) ppm. ¹⁹F NMR data (C₆D₅Br, 282.3 MHz, 293 K): -131.81 (8 F, br d, *o*-C₆F₅, ${}^{3}J$ = 10.6 Hz), -162.05 (4 F, t, *p*-C₆F₅, ${}^{3}J$ = 21.2 Hz), -165.94 (8 F, m, *m*-C₆F₅) ppm. ¹¹B NMR data (C₆D₅Br, 96.3 MHz, 293 K): -15.9 ppm.

MeN(CH₂CH₂CH₂N(mesityl)H)₂

¹H NMR data (benzene-d₆, 300.1 MHz, 293K): 6.81 (4 H, s, $C_{6H_2}Me_3$), 3.11 (2H, br t, $NH_{...}{}^{3}J = 7.0$ Hz), 2.91 (4 H, q, $ArNCH_{2}$, ${}^{3}J = 7.0$, 6.8 Hz), 2.27 (4 H, t, $MeNCH_{2}$, ${}^{3}J = 6.8$ Hz), 2.22 (12 H, s, *o*- $C_{6}H_{2}Me_{3}$), 2.19 (6 H, s, *p*- $C_{6}H_{2}Me_{3}$), 2.04 (3 H, s, NMe), 1.59 (4 H, quin, $CH_{2}CH_{2}CH_{2}$, ${}^{3}J = 6.8$ Hz) ppm. ${}^{13}C\{{}^{1}H\}$ NMR data (benzene-d₆, 125.7 MHz, 293K): 144.5 (Cq of $C_{6}H_{2}Me_{3}$), 130.9 (Cq of $C_{6}H_{2}Me_{3}$), 129.9 (*m*- $C_{6}H_{2}Me_{3}$), 129.8 (Cq of $C_{6}H_{2}Me_{3}$), 56.6 (MeN<u>C</u>H₂), 47.7 (ArN<u>C</u>H₂), 42.1 (NMe), 28.9 (CH₂<u>C</u>H₂CH₂), 20.8 (*p*- $C_{6}H_{2}Me_{3}$), 18.6 (*o*- $C_{6}H_{2}Me_{3}$) ppm. IR data (NaCl plates, film): 3314 (m, br.) (v(NH)), 2940 (s), 2794 (s), 1727 (w), 1592 (w), 1485 (s), 1372 (m), 1303 (m), 1231 (s), 1182 (m), 1153 (s), 1136 (m), 1101 (m), 1031 (m), 1012 (m), 960 (w), 933 (w), 853 (s), 735 (m), 697 (m), 582 (m), 563 (m) cm⁻¹. HR EI-MS for [MeN(CH₂CH₂CH₂N(H)Mes)₂]⁺, found (calc. for C₁₃H₃₅N₃Si₂): *m/z* = 381.3150 (381.3144).). Anal. Found (calc. for C₂₅H₃₉N₃): C 78.7.8 (78.7), H 10.2 (10.3), N 10.6 (11.0) %.

Synthesis of the new ligands

[MeN(CH₂CH₂CH₂N(H)SiMe₃)₂]₂ (1-H₂)

3,3'-diamino-N-methyldipropylamine (9.0 g, 10.0 mL, 62.0 mmol) and triethylamine (25.1 g, 34.6 mL, 248 mmol, 4 eq) were dissolved in THF (100 mL) and cooled to 0 °C for the dropwise addition of B412381F ESI - page 5

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chlorotrimethylsilane (14.8 g, 17.3 mL, 136 mmol, 2.2 eq), upon which a large quantity of white precipitate formed. The reaction was stirred at rt for 3 h before the precipitate was removed by filtration. The volatiles were removed under reduced pressure and the resulting colourless oil extracted into pentane (30 mL). The solvent was removed under reduced pressure to afford $H_2N_2N^{3,Me}$ as a colourless oil in 84% yield (15.2 g, 52.0 mmol).

MeN(CH₂CH₂CH₂N(mesityl)H)₂

3,3'-diamino-N-methyldipropylamine (2.0 g, 2.2 mL, 13.8 mmol), mesityl bromide (5.5 g, 27.5 mmol, 2 eq), sodium *tert* butoxide (4.0 g, 41.3 mmol, 3 eq), racemic-2,2'-bis(diphenylphosphino)-1,1'-binapthyl (0.3 g, 0.5 mmol, 0.038 eq) and tris(dibenzylideneacetone)dipalladium(0) (0.2 g, 0.2 mmol, 0.015 eq) were dissolved in toluene (80 mL) and refluxed at 110°C under a flow of N_2 for 24 h. The volatiles were removed under reduced pressure and the resulting blood red residue redissolved in diethyl ether (100 mL) and extracted by filtration from a grey solid. The solid was washed with diethyl ether (3 x 20 mL) and the ether fractions were combined and washed with water (3 x 75 mL) and saturated aqueous NaCl solution (3 x 75 mL) and dried over magnesium sulphate. The volatiles were removed under reduced pressure to give a red oil which was further purified by distillation at 240°C and 2 x 10⁻¹ mbar affording a yellow oil in 46 % yield (2.4 g, 6.3 mmol).

General procedures for the polymerisation experiments

MAO activation of dichloride complexes

To a sealable metal reactor, containing a glass insert, was added MAO (20 mL, 10 % in toluene w/w: 30 mmol, 1500 eq) dissolved in toluene (180 mL). All transfers were made under vacuum line pressure of either dry argon or ethylene. The solution was stirred at 250 rpm for 5 min to remove any water or impurities. The pre-catalyst (20 µmol) was dissolved in toluene (50 mL) and added to the reactor. The pre-

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catalyst was activated by stirring with MAO solution for 30 min at 250 rpm. The reaction vessel was placed under full vacuum for 10 s, the stirring was increased to 750 rpm and the temperature recorded. The reactor was placed under a dynamic pressure of 5 bar of ethylene and reaction temperature monitored.

After 60 min, the reactor was isolated and the pressure released. Methanol (50 mL) was added to the mixture, followed by water (50 mL) (with stirring). The mixture was stirred for 12 h in conc. HCl (100 mL). The precipitated polymers were filtered, washed with water (1000 ml) and dried to constant weight.

[Ph₃C][BAr^F₄]/AlⁱBu₃ activation of dialkyl complexes

To a sealable metal reactor, containing a glass insert, was added AlⁱBu₃ (5 ml, 5 mmol) dissolved in toluene (200 ml). All transfers were made under vacuum line pressure of either dry argon or ethylene. The solution was stirred at 250 rpm for 5 min to remove any water or impurities. The pre-catalyst (20 μ mol) was dissolved in toluene (25 ml) and added to the reactor and stirred for 5 min. The co-catalyst [Ph₃C][BAr^F₄] (20 μ mol) was dissolved in toluene (20 ml) and added to the reactor. The reaction vessel was placed under full vacuum for 10 s, the stirring was increased to 750 rpm and the temperature recorded. The reactor was placed under a dynamic pressure of 5 bar of ethylene and reaction temperature monitored every 5 min. After 60 min, the reactor was isolated and the pressure released. Methanol (50 ml) was added to the mixture, followed by water (50 ml) (with stirring). The mixture was acidified to pH1 using a solution of 10 % HCl in MeOH and stirred for 12 h. The precipitated polymers were filtered, washed with water (1000 ml) and dried to constant weight.