Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Organoselenium Compounds: Development of a Universal "Living" Free Radical Polymerization Mediator

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Synthesis of organoselenium compounds.

Procedures for the synthesis of cyanomethyl diethylcarbamodiselenoate (N1).[1] Diethylamine (0.22 g, 6 mmol) was dissolved in THF (10 mL), and a solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. Then, a solution of $BrCH_2CN$ (0.36 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with ethyl acetate/n-hexane (1:5) to afford the product in 85% yield. ^1H NMR ($CDCl_3$, δ, ppm): 1.34 (t, 3H,

CH_3), 1.36 (t, 3H, CH_3), 3.72 (m, 2H, CH_2), 4.15 (m, 2H, CH_2), 4.19 (s, 2H, CH_2CN); ^{13}C NMR ($CDCl_3$, δ, ppm): 11.88, 20.62, 12.82, 51.07, 54.97, 117.70, 189.66; LCMS (ESI) m/z:$[M + H]^+$ calcd. for $C_7H_{12}N_2Se_2$, 284.93 (100%), 282.93 (82.1%), 280.94 (33.9%); found: 284.9385, 282.9398, 280.9405; HPLC: 98.6%.

Procedure for the synthesis of Se-cyanomethyl O-ethyl carbonodiselenoate (O1). Ethanol (3 mL) was stirred with NaOH (0.12 g, 3 mmol) at 0 ^oC. A solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. Then, a solution of $BrCH_2CN$ (0.36 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with ethyl acetate/hexane (1:10) to afford the product in 78% yield. ^1H NMR ($CDCl_3$, δ, ppm): 1.58 (t, 3H, CH_3), 3.75 (s, 2H, CH_2CN), 4.87 (m, 2H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 8.46, 8.72, 70.69, 111.12, 208.71; LCMS (ESI) m/z: $[M + Na]^+$calcd. for $C_5H_7NOSe_2$, 279.89 (100%), 277.89 (88.9%), 275.89 (53.0%); found: 279.8775, 277.8786, 275.8793; HPLC: 99.7%.

Procedure for the synthesis of Se-cyanomethyl O-phenyl carbonodiselenoate (O2). Phenol (0.30 g, 3 mmol) was dissolved in THF (10 mL) and stirred with NaOH (0.12 g, 3 mmol) at 0 ^oC. A solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. Then, a solution of $BrCH_2CN$ (0.36 g, 3 mmol) and THF (2 mL) was added at 0 ^oC over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with ethyl acetate/hexane (1:10) to afford the product in 65% yield. ^1H NMR ($CDCl_3$, δ, ppm): 3.88 (s, 2H, CH_2), 7.20-7.50 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 15.76, 116.29, 121.92, 127.64, 127.73 130.20, 166.70, 214.27; LCMS (ESI) m/z: $[M + H]^+$ calcd. for $C_9H_7NOSe_2$, 305.89 (100%), 303.89 (89.6%) 301.89 (53.3%); found: 305.8931, 303.8935, 301.8951; HPLC: 98.5%.

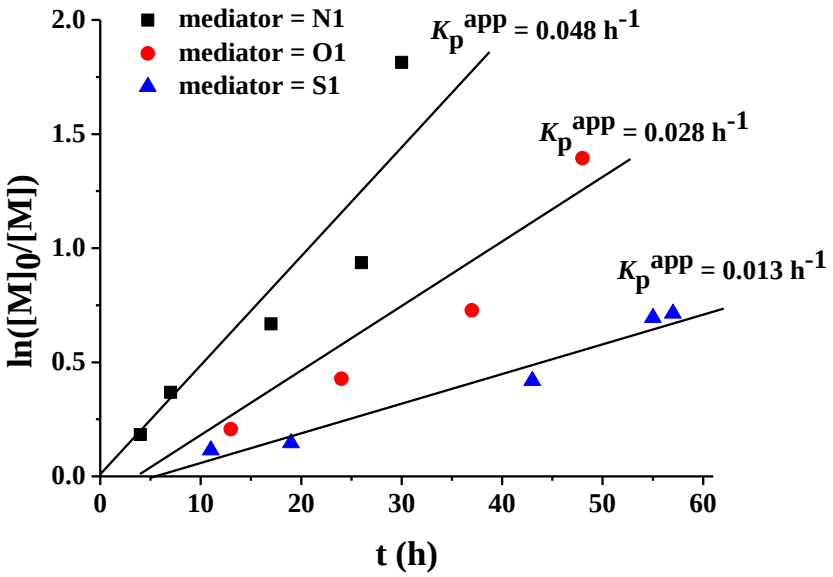
Procedure for the synthesis of ethyl 2-(phenoxycarbonoselenoylselanyl)acetate (O3). Phenol (0.3 g, 3 mmol) was dissolved in THF (10 mL) and stirred with NaOH (0.12 g, 3 mmol) at 0 ^{o}C. A solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 ^{o}C over 3 min. Then, a solution of $BrCH_2COOC_2H_5$ (0.36 g, 3 mmol) and THF (2 mL) was added at 0 ^{o}C over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with ethyl acetate/hexane (1:10) to afford the product in 60% yield. ^{1}H NMR (CDCl3, δ, ppm): 1.29 (t, 3H, CH_3), 4.05 (s, 2H, $SeCH_2$), 4.23 (m, 2H, CH_2C), 7.15-7.45 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 11.93, 32.80, 59.63, 119.59, 124.69, 127.42, 154.27, 163.26, 215.48; LCMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{11}H_{12}O_3Se_2$, 374.91 (100%), 372.91 (87.7%), 370.91 (52.0%); found: 374.9018, 372.9022, 370.9031; HPLC: 98.2%.

Procedure for the synthesis of methyl 2-(phenoxycarbonoselenoylselanyl)-2-phenylacetate (O4). Phenol (0.3 g, 3 mmol) was dissolved in THF (10 mL) and stirred with NaOH (0.12 g, 3 mmol) at 0 ^{o}C. A solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 ^{o}C over 3 min. Then, a solution of $BrCH(Ph)COOCH_3$ (0.69 g, 3 mmol) and THF (2 mL) was added at 0 ^{o}C over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with ethyl acetate/hexane (1:10) to afford the product in 48% yield. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.77 (s, 3H, OCH_3), 5.66 (s, 1H, CH), 7.00-7.70(m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$, δ, ppm): 53.20, 55.52, 120.91, 121.91, 127.10, 128.75, 129.01, 129.79, 134.47, 156.34, 170.23, 217.98; LCMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{16}H_{14}O_3Se_2$, 436.93 (100%), 434.93 (90.3%), 432.93 (53.4%); found: 436.9171, 434.9177, 432.9182; HPLC: 98.6%.

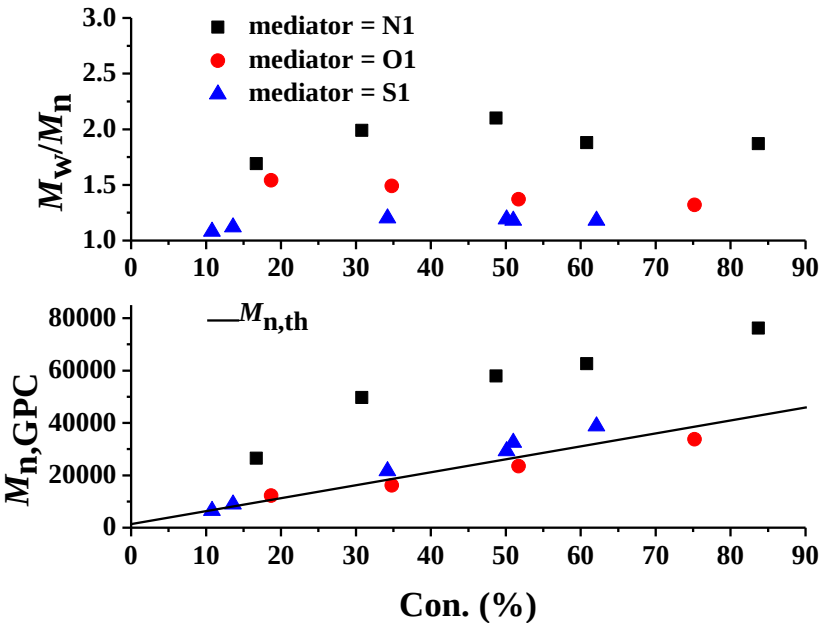
Procedures for Synthesis of Se-cyanomethyl S-ethyl carbonodiselenothioate (S1). Ethanethiol (0.53 g, 3 mmol) was dissolved in THF (10 mL) and stirred with NaOH (0.12 g, 3 mmol) at 0 ^{o}C. A

solution of CSe_2 (0.53 g, 3 mmol) and THF (2 mL) was added at 0 °C over 3 min. Then, a solution of $BrCH_2CN$ (0.69 g, 3 mmol) and THF (2 mL) was added at 0 °C over 3 min. After stirring for 15 min, the mixture was extracted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography on silica eluting with hexane to afford the product 55% yield. ^1H NMR ($CDCl_3$, δ, ppm): 4.00 (s, 2H，CH_2CN), 3.47 (m, 2H, CH_2), 1.47 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 9.86, 13.71, 34.64, 113.65, 213.59; LCMS (ESI) m/z: $[M + Na]^+$calcd. for $C_5H_7NSSe_2$, 295.86 (100%), 293.86 (81.2%), 291.86 (33.3%); found: 295.8553, 293.8562, 291.8567; HPLC: 98.1%.

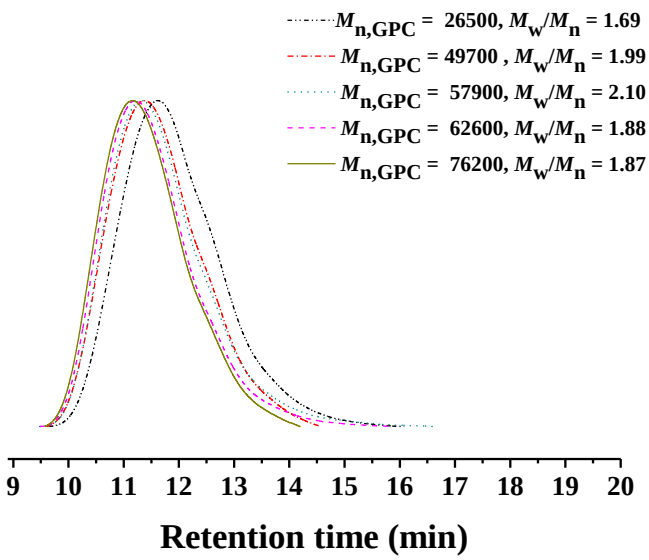
Polymerization



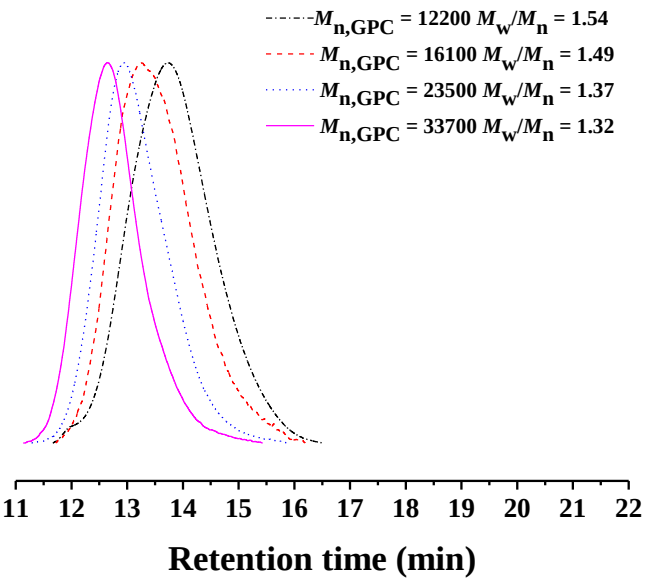
FS 1. ln($[M]_0$/[M]) as a function of time for the polymerization of styrene in the presence of N1, O1, and S1 with a molar ratio of $[St]_0$:[seleno-mediator]$_0$:$[AIBN]_0$=500:1:0.5 in bulk at 60 °C. $[St]_0$ = 8.74 mol/L, [seleno-mediator]$_0$ = 0.0175 mol/L, $[AIBN]_0$ = 0.0087 mol/L.



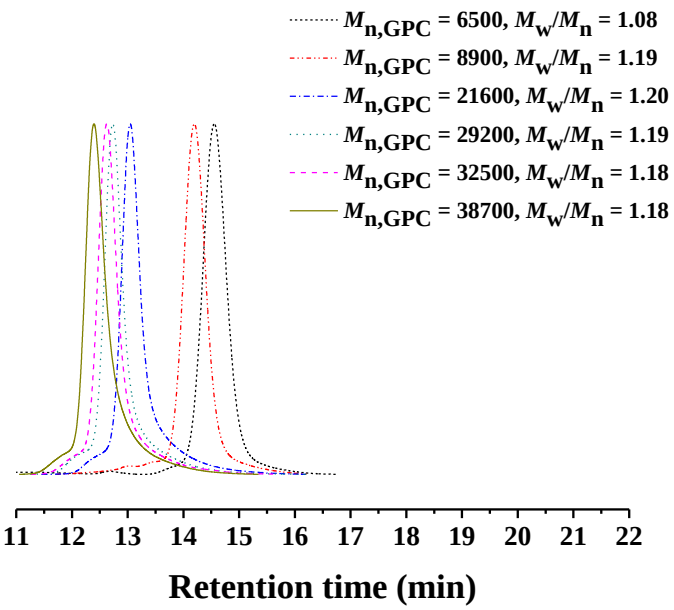
FS 2. Dependence of M_n and M_w / M_n on the conversion of styrene in the presence of N1, O1, and S1 with a molar ratio of $[St]_0$:$[seleno\text{-}mediator]_0$:$[AIBN]_0$=500:1:0.5 in bulk at 60 °C.



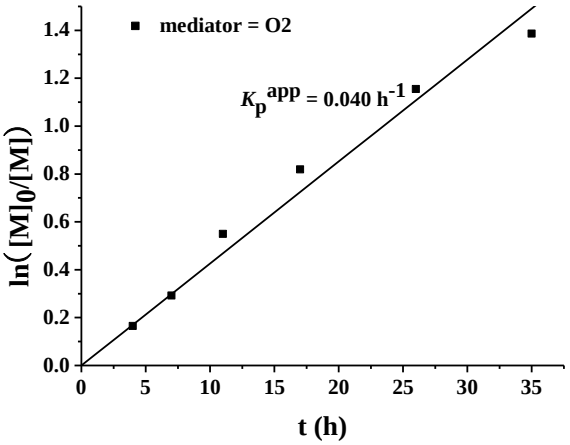
FS 3. Evolution of GPC traces of the prepared PS-N1 obtained from N1 mediated polymerization of styrene with a molar ratio of $[St]_0$:$[N1]_0$:$[AIBN]_0$ = 500:1:0.5 under bulk condition at 60 °C.



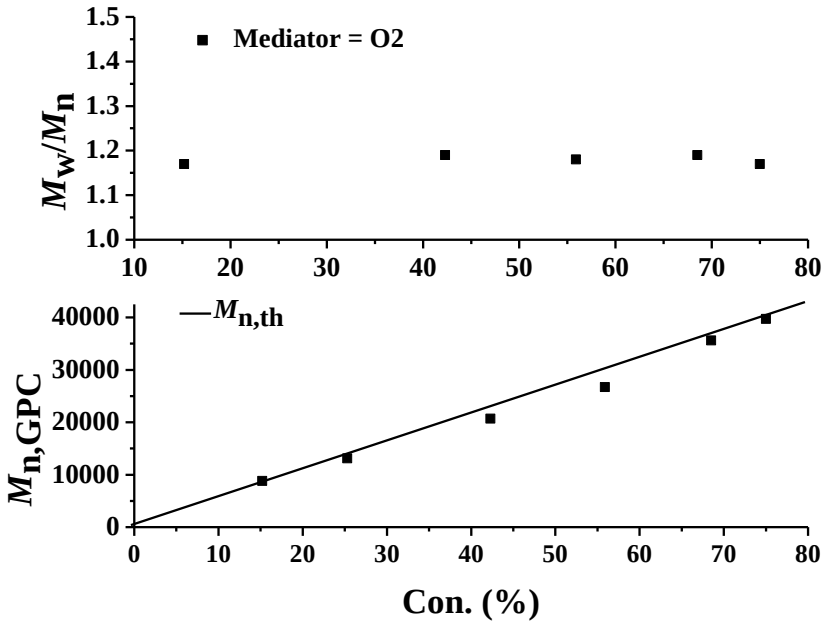
FS 4. Evolution of GPC traces of the prepared PS-O1 obtained from O1 mediated polymerization of styrene with a molar ratio of $[St]_0:[O1]_0:[AIBN]_0 = 500:1:0.5$ under bulk condition at 60 ^oC.



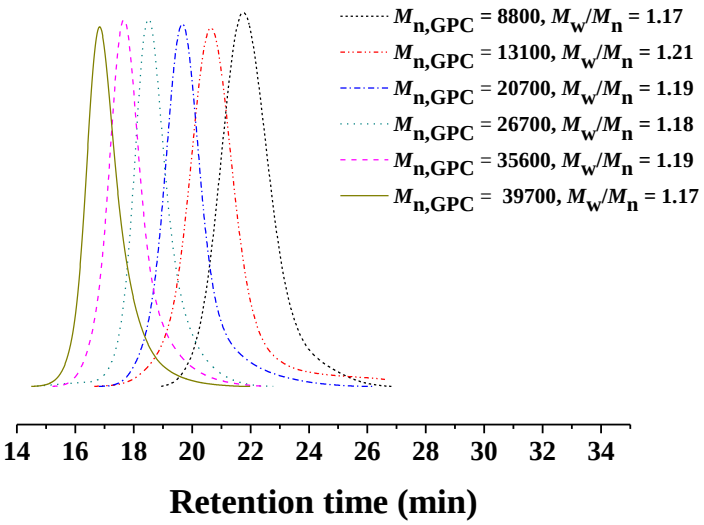
FS 5. Evolution of GPC traces of the prepared PS-S1 obtained from S1 mediated polymerization of styrene with a molar ratio of $[St]_0:[S1]_0:[AIBN]_0 = 500:1:0.5$ under bulk condition at 60 ^oC.



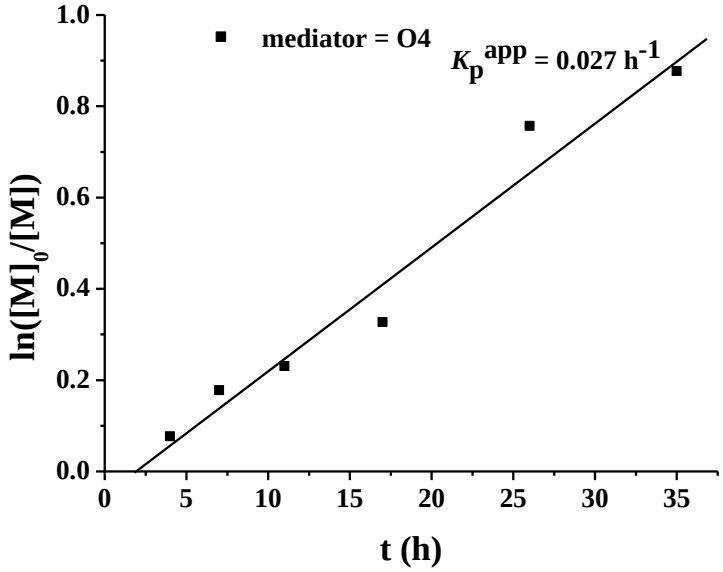
FS 6. ln([M]$_0$/[M]) versus time for the polymerization of styrene in the presence of O2 with the molar ratio of [St]$_0$:[O2]$_0$:[AIBN]$_0$=500:1:0.5 in bulk at 60 ^{o}C.



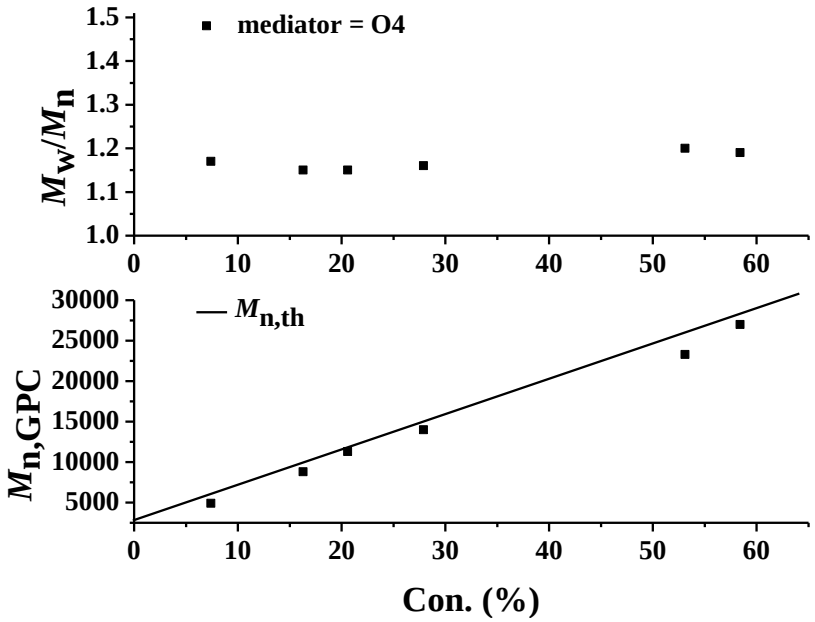
FS 7. Dependence of M_n and M_w / M_n on conversion of styrene in the presence of O2 with the molar ratio of [St]$_0$:[O2]$_0$:[AIBN]$_0$=500:1:0.5 in bulk at 60 ^{o}C. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8×300 mm, 5 μm beads size) columns with molecular weights ranging from 10^2 ~ 5×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 30 ^{o}C.



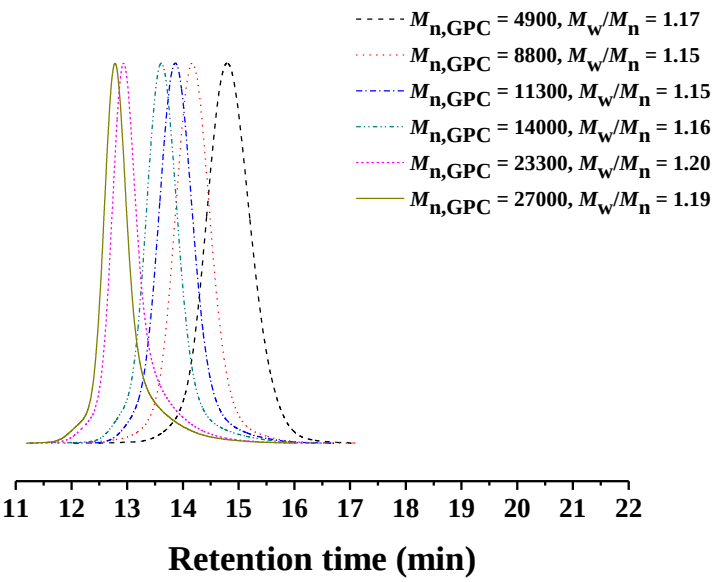
FS 8. Evolution of GPC traces of the prepared PS-O2 obtained from O2 mediated polymerization of styrene with the molar ratio of $[St]_0:[O2]_0:[AIBN]_0 = 500:1:0.5$ under bulk condition at 60^oC.



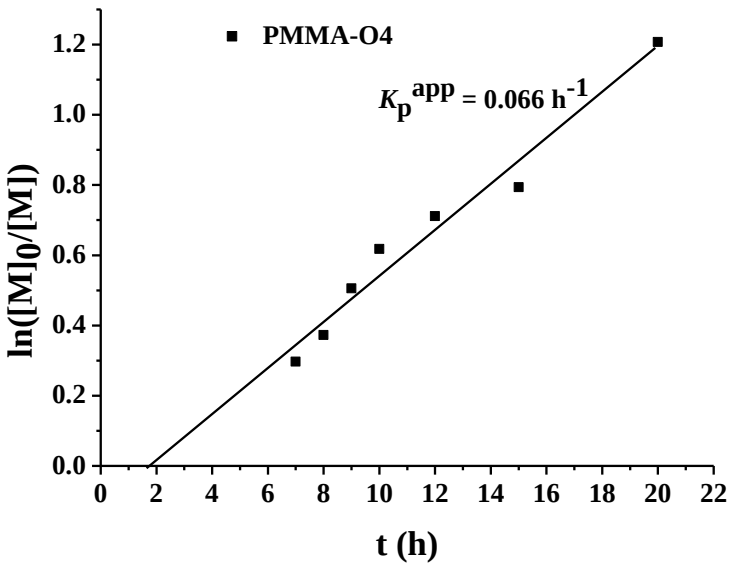
FS 9. ln([M]$_0$/[M]) as a function of time for the polymerization of styrene in the presence of O4 with a molar ratio of [St]$_0$:[O4]$_0$:[AIBN]$_0$=500:1:0.5 in bulk at 60 ^{o}C. [St]$_0$ = 8.74 mol/L, [O4]$_0$ = 0.0175 mol/L, [AIBN]$_0$ = 0.0087 mol/L.



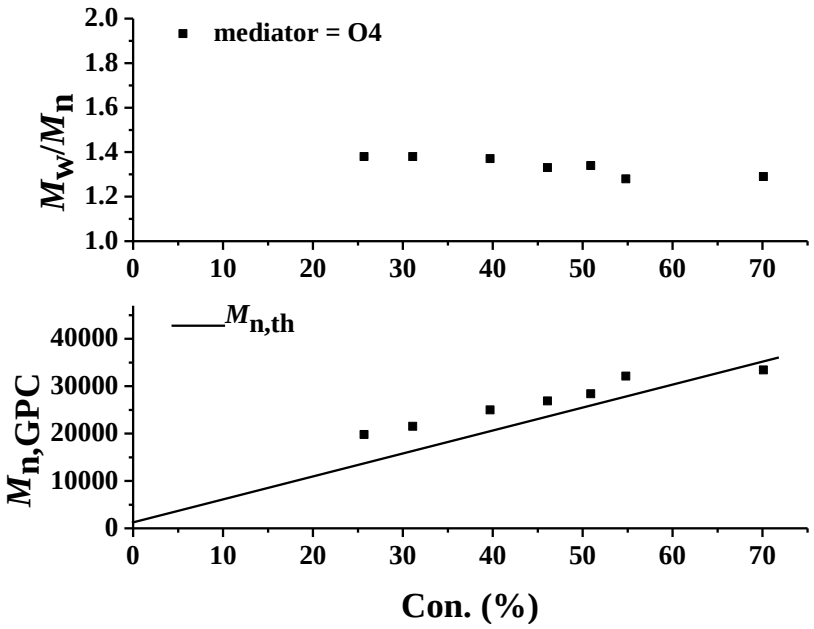
FS 10. Dependence of M_n and M_w / M_n on the conversion of styrene in the presence of O4 with a molar ratio of [St]$_0$:[seleno-mediator]$_0$:[AIBN]$_0$=500:1:0.5 in bulk at 60 ^{o}C.



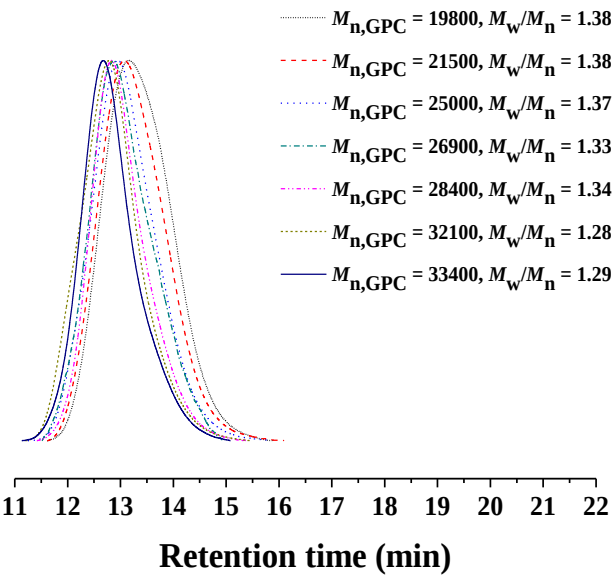
FS 11. Evolution of GPC traces of the prepared PS-O4 obtained from O4 mediated polymerization of St with a molar ratio of $[St]_0:[O4]_0:[AIBN]_0 = 500:1:0.5$ under bulk condition at 60 °C.



FS 12. $\ln([M]_0/[M])$ as a function of time for the polymerization of MMA in the presence of O4 with a molar ratio of $[MMA]_0:[O4]_0:[AIBN]_0=500:1:0.5$ in bulk at 60 °C. $[MMA]_0$ = 9.47 mol/L, $[O4]_0$ = 0.0189 mol/L, $[AIBN]_0$ = 0.0095 mol/L.



FS 13. Dependence of M_n and M_w / M_n on the conversion of MMA in the presence of O4 with a molar ratio of $[MMA]_0:[O4]_0:[AIBN]_0=500:1:0.5$ in bulk at 60 °C.



FS 14. Evolution of GPC traces of the prepared PMMA-O4 obtained from O4 mediated polymerization of MMA with a molar ratio of $[MMA]_0:[O4]_0:[AIBN]_0$ = 500:1:0.5 under bulk condition at 60 °C.

It showed that, in the presence of N1, the molecular weights were higher than theorical one and the molecular weight distributions were broad (FS 2 and FS 3), which is similar to its thiocarbonylthio analogues (i.e., diethylcarbamodithioates).[2] In case of O1, the molecular weights of the prepared polystyrene (PS) determined by GPC were close to the theoretical values with relatively narrow molecular weight distributions in the range of 1.32-1.54 (FS 2 and FS 4). Compared with its thiocarbonylthio analogues (i.e., O-ethyl carbonodithioates), which was classical RAFT agents for polymerization of vinyl acetate, was rarely applied in the polymerization of St.[3] In case of S1, the molecular weights of the obtained PS determined by GPC were close to the theoretical values with narrow molecular weight distributions in the range of 1.08-1.19 (FS 2 and FS 5), and the thiocarbonylthio analogues (i.e., alkyl carbonotrithioates) were also good RAFT agents for polymerization of St and other conjugated monomers.[4] The results shown in FS 8, FS 10, and FS 11 indicated that O2 and O4 controlled the polymerization of styrene by the linear increase in the number-average molecular weight as a function of the monomer conversion, the agreement between the experimental molecular weights, and the predicted values and the narrow molecular weight distributions that were in the range of 1.17-1.21 and 1.15-1.20. In addition, the thiocarbonylthio analogues (i.e., O-phenyl carbonodithioates) were not good RAFT agents for polymerization of St.[2] In the presence of O4, the molecular weights of the obtained PMMA determined by GPC were close to the theoretical values with narrow molecular weight distributions in the range of 1.28-1.38 (FS 13 and FS14).

Reference

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