

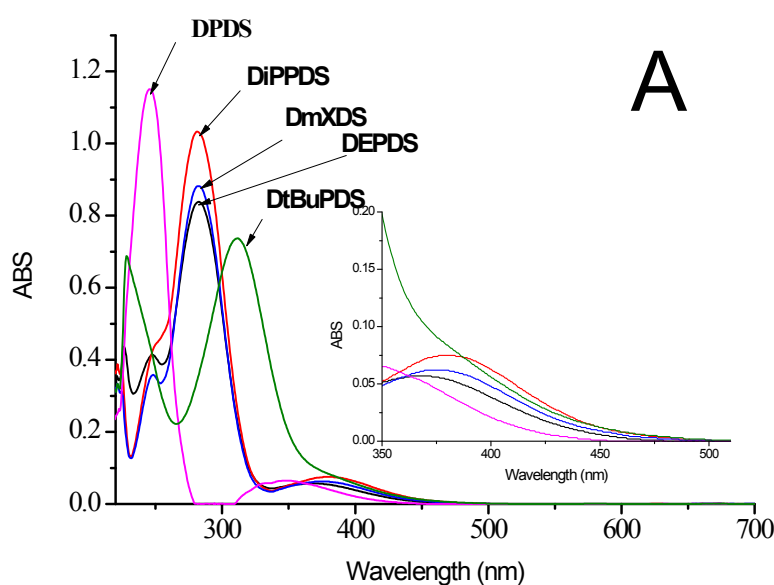
Supporting Information

Diselenides Mediated Controlled Radical Polymerization Under Visible Light Irradiation: Mechanism Investigation and α , ω -Ditelechelic Polymers

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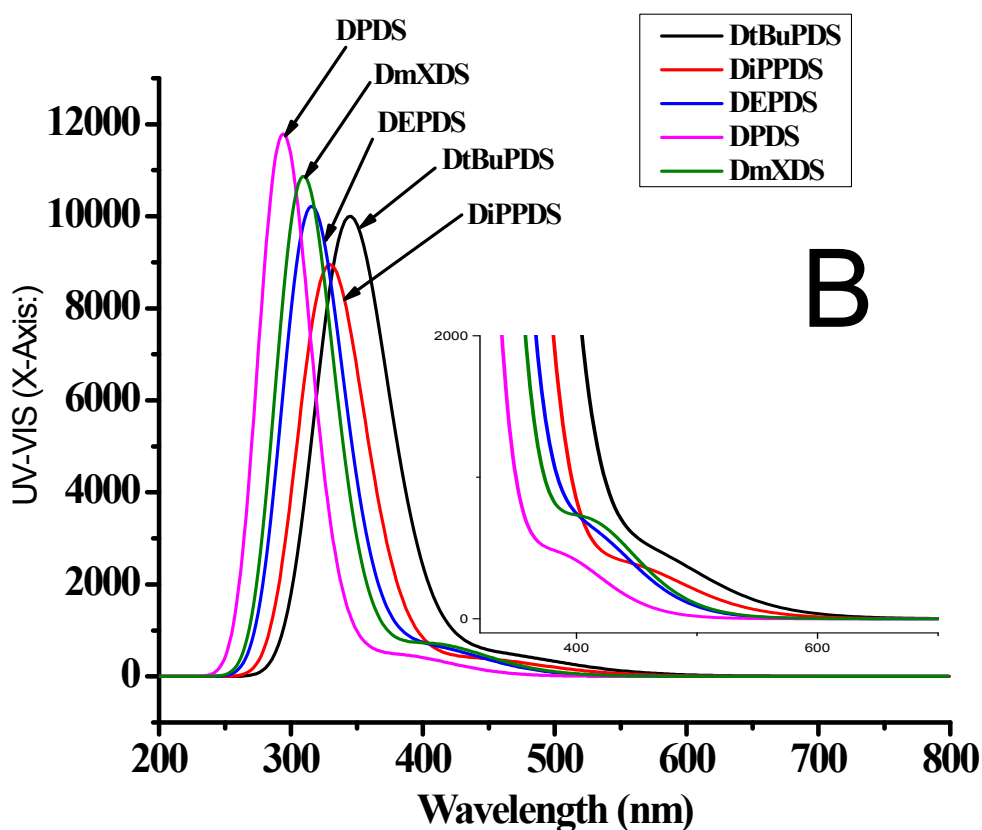
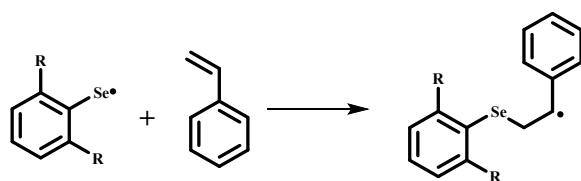


Figure 1S. A) The UV-vis spectra of diselenide compounds with different substitution groups on benzene ring in toluene with the concentration of 1×10^{-4} mol/L. B) The UV-vis spectra of diselenides with different substitution groups obtained from time-dependent (TD) DFT calculation.

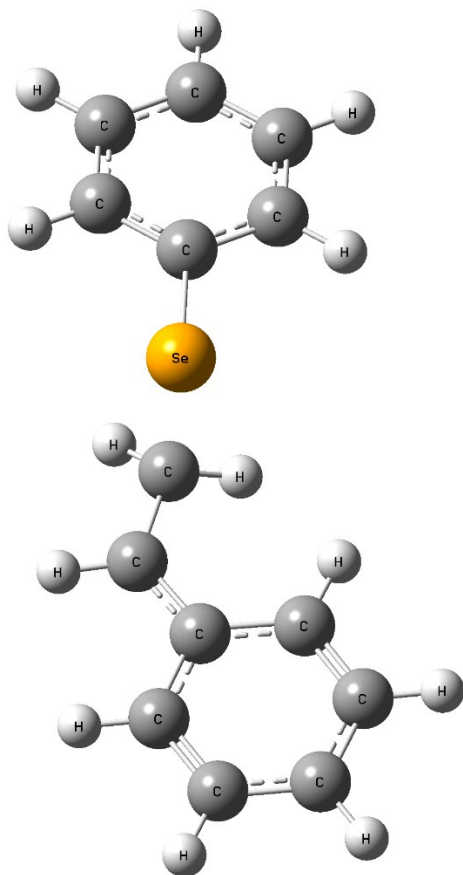
Table 1S. The Gibbs free energy of the radical adding with styrene.



No.	Mother structure of radical	Gibbs free energy (Kcal/mol)
1	DPDS	2.95
2	DmXDS	6.66
3	DEPDS	12.11
4	DiPPDS	11.64
5	DtBuPDS	13.72

Minimal structure of radicals generated from diselenide with styrene: calculated using the three parameter hybrid B3LYP density functional method with the extended basis set 6-311++G(d,p) implemented in the GAUSSIAN 09 package.

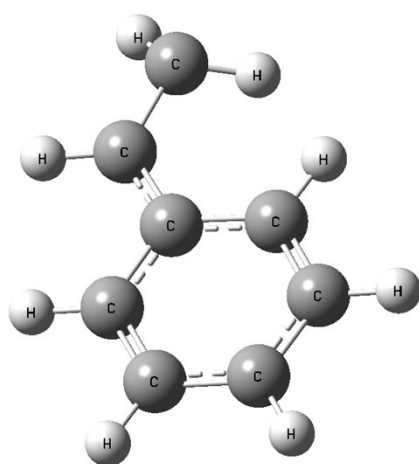
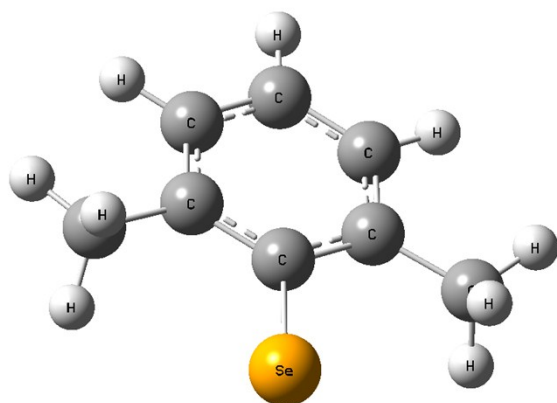
A). DPDS derived radical with styrene:



C	5.22046500	-0.46222900	-0.09175800
C	4.02222600	-1.09949500	-0.35857700
C	2.80478500	-0.37154100	-0.46612500
C	2.87014800	1.03614000	-0.27572900
C	4.07501000	1.66335100	-0.00626700
C	5.25900000	0.92517800	0.08515300
H	6.13377000	-1.04223900	-0.01778900
H	3.99888800	-2.17577000	-0.49381900
H	1.96325300	1.62618600	-0.32522200
H	4.09775800	2.73784300	0.13893700

H	6.19822800	1.42331000	0.29539700
C	1.59883100	-1.05861900	-0.75823600
H	1.64560700	-2.14196500	-0.80819800
C	0.27826500	-0.44529300	-0.91539600
H	-0.38536900	-1.04361900	-1.53613800
H	0.30087800	0.58136300	-1.27379600
Se	-0.69709000	-0.37449800	0.90249100
C	-2.48099700	0.00103700	0.23848800
C	-3.34942500	-1.04827600	-0.07867400
C	-2.91375500	1.32296300	0.09495200
C	-4.63534900	-0.77557600	-0.54123900
H	-3.01836600	-2.07265900	0.04362700
C	-4.20124800	1.59056800	-0.36658300
H	-2.24514000	2.13630000	0.35031500
C	-5.06276800	0.54296100	-0.68622800
H	-5.30411300	-1.59413200	-0.78355400
H	-4.53090600	2.61812400	-0.47360100
H	-6.06456400	0.75317700	-1.04352100

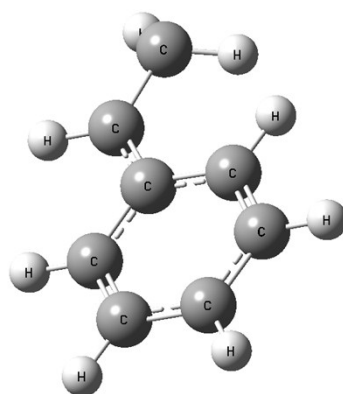
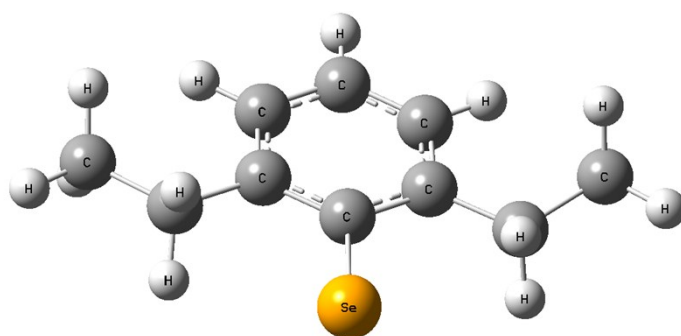
B) DmXDS derived radical with styrene:



C	-5.45051200	-0.79054600	0.25164900
C	-4.19236900	-1.14974400	0.70017500
C	-3.08203100	-0.26964400	0.57321600
C	-3.31863800	0.98901100	-0.04475600
C	-4.58206100	1.33714000	-0.49292300
C	-5.65816400	0.45653800	-0.34794400
H	-6.27917700	-1.48104200	0.36375000
H	-4.03788600	-2.11907200	1.16250000
H	-2.49801100	1.68269700	-0.18134700
H	-4.73517600	2.30172400	-0.96440800
H	-6.64405800	0.73605300	-0.70057200

C	-1.80963700	-0.66799800	1.05824900
H	-1.71884300	-1.68031100	1.43896100
C	-0.58488400	0.13088200	1.00239500
H	0.13541600	-0.15310500	1.76651200
H	-0.75282000	1.20456300	1.02478400
Se	0.42110200	-0.26387500	-0.76010100
C	2.25970700	0.01035500	-0.17362000
C	3.11658000	-1.10742800	-0.07814100
C	2.73016600	1.31118700	0.10441600
C	4.44347100	-0.89709400	0.30993000
C	2.66200300	-2.51538000	-0.38316300
C	4.06386900	1.46889000	0.49494200
C	1.85574400	2.53702700	-0.00416600
C	4.91588300	0.37709500	0.59883300
H	5.11010100	-1.74941800	0.38700600
H	1.78440200	-2.79061100	0.20597800
H	2.37882700	-2.62898100	-1.43317000
H	3.46235100	-3.22691100	-0.17081000
H	4.43440200	2.46541200	0.71096400
H	1.26509700	2.52378200	-0.92237400
H	1.15106200	2.60275700	0.83086400
H	2.46406600	3.44332800	0.01054500
H	5.94803200	0.51914300	0.89968200

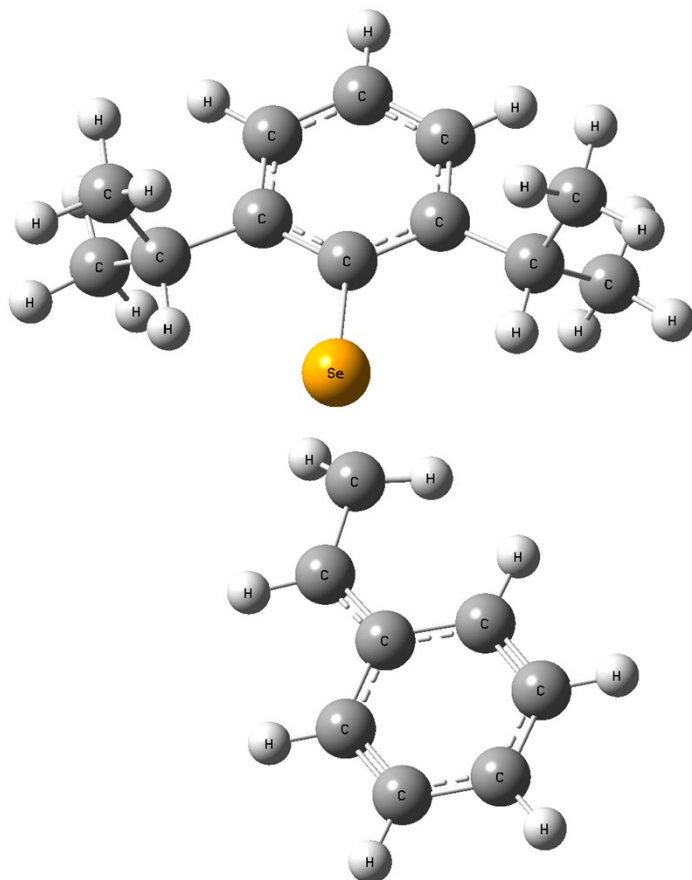
C) DEPDS derived radical with styrene:



C	-5.72093800	-0.95006300	0.33258300
C	-4.44568200	-1.20857300	0.80156700
C	-3.38016900	-0.28925300	0.59473100
C	-3.67973100	0.90024300	-0.12446500
C	-4.95956500	1.14703300	-0.59319600
C	-5.99091000	0.23039000	-0.36837100
H	-6.51448600	-1.66816800	0.50773300
H	-4.24301900	-2.12679800	1.34286300
H	-2.89467500	1.62003500	-0.32273900
H	-5.16066400	2.05991600	-1.14310700
H	-6.98999000	0.43088500	-0.73727500
C	-2.08867500	-0.58332400	1.10352500
H	-1.94569700	-1.55660500	1.56202100
C	-0.90795600	0.27135700	0.98018400

H	-1.13212800	1.33348500	0.92203500
H	-0.17136300	0.08415200	1.75853900
Se	0.11496100	-0.20323800	-0.75372300
C	1.95888200	0.02702000	-0.15383900
C	2.78317600	-1.11853200	-0.05525600
C	2.45724000	1.31900900	0.12855100
C	4.11021900	-0.94086800	0.34657400
C	2.25744000	-2.50906200	-0.37999800
C	3.79029400	1.43709500	0.53573400
C	1.58508400	2.55700700	0.00070900
C	4.60815100	0.32112200	0.64528300
H	4.76505000	-1.79830300	0.43128300
H	1.35434600	-2.68348300	0.21279700
H	1.91092000	-2.51911300	-1.41888300
C	3.23002500	-3.67273900	-0.17454400
H	4.19766100	2.41429600	0.76086800
H	0.96875000	2.44529300	-0.89572800
H	0.87604300	2.57663900	0.83689000
C	2.31526000	3.90252600	-0.04930600
H	5.64001300	0.43484600	0.95954100
H	2.73514700	-4.61396700	-0.42633200
H	4.11417800	-3.58716500	-0.81220000
H	3.56779800	-3.74551200	0.86309000
H	3.04879800	3.93078100	-0.85966400
H	1.59613000	4.70702300	-0.22282700
H	2.83563200	4.12952700	0.88488700

D) DiPDS derived radicals with styrene:

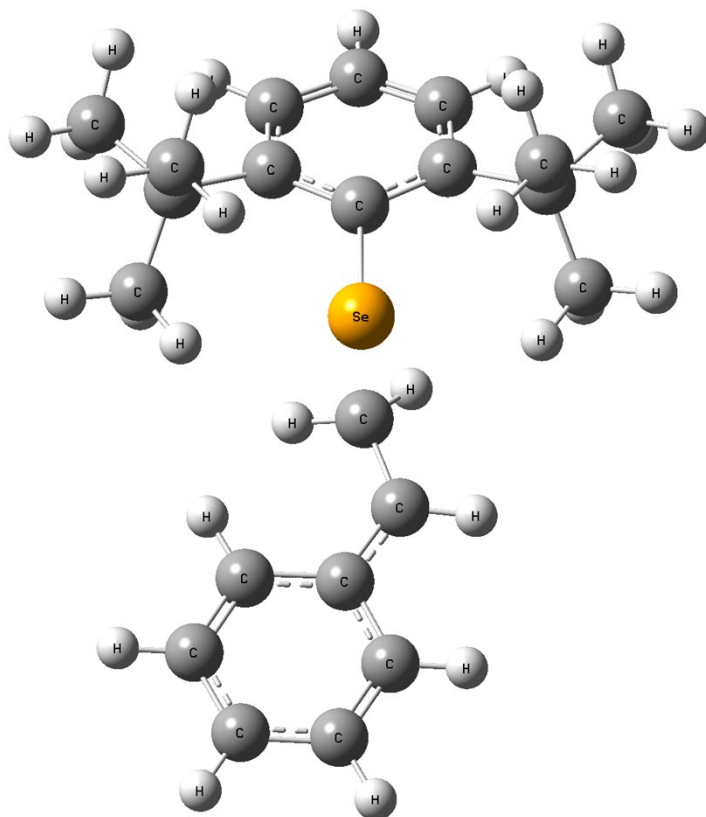


C	5.90151700	-1.00311100	0.00963500
C	4.65990700	-1.52855400	-0.29917500
C	3.52045900	-0.69186200	-0.45910100
C	3.71117500	0.70573800	-0.27886300
C	4.95838400	1.22086600	0.03240200
C	6.06340300	0.37651300	0.17730800
H	6.75279400	-1.66513400	0.12380300
H	4.54103800	-2.59947700	-0.42639300
H	2.86819200	1.37894800	-0.37427100
H	5.07647000	2.29036100	0.16811400

H	7.03632400	0.78720600	0.42062500
C	2.26722500	-1.26790300	-0.78941000
H	2.21849900	-2.35127700	-0.83742900
C	1.01112100	-0.54071600	-0.98614000
H	1.13415400	0.48112900	-1.33905200
H	0.31973800	-1.07536400	-1.63425700
Se	-0.01236300	-0.39450600	0.79849200
C	-1.76250500	0.14103000	0.09692400
C	-2.03721600	1.51263800	-0.11869200
C	-2.75054500	-0.84575000	-0.13765800
C	-3.31866200	1.87122400	-0.55088400
C	-1.02305700	2.62721500	0.12399000
C	-4.01460900	-0.42625100	-0.56598600
C	-2.52116000	-2.33796000	0.08781500
C	-4.30075400	0.91619200	-0.77013700
H	-3.55095300	2.91770600	-0.71312100
C	-1.38899000	3.44148100	1.37870500
H	-0.06071700	2.15351700	0.32227800
C	-0.84771200	3.54282500	-1.10094800
H	-4.78852500	-1.16463700	-0.74082300
C	-3.17982800	-2.79868000	1.40167400
H	-1.44640900	-2.48644700	0.20061300
C	-2.98533700	-3.20149300	-1.09806300
H	-5.28883400	1.21750600	-1.10093200
H	-2.35462600	3.94232700	1.26049100
H	-1.45068700	2.79757800	2.25938300
H	-0.63332400	4.20896300	1.57167600

H	-0.04529100	4.26404200	-0.91918600
H	-0.59094000	2.96807400	-1.99483100
H	-1.75410800	4.11359900	-1.32244400
H	-4.26513100	-2.66154800	1.37004200
H	-2.97842700	-3.85907300	1.58168500
H	-2.79518300	-2.23166500	2.25297900
H	-4.07092800	-3.17862700	-1.22950600
H	-2.52936500	-2.87043600	-2.03496300
H	-2.70029900	-4.24472000	-0.93358300

E) DtBuPDS derived radical with styrene:



C	-5.99121200	-1.03864000	-0.05029000
C	-4.72593200	-1.53232900	-0.31601300
C	-3.61620500	-0.66229800	-0.50880100
C	-3.86242100	0.73483600	-0.40954600
C	-5.13284400	1.21854500	-0.14091300
C	-6.20749200	0.34146600	0.03929800
H	-6.81827300	-1.72579800	0.09059000
H	-4.56551400	-2.60342700	-0.38214600
H	-3.04630700	1.43503700	-0.53754500
H	-5.29276200	2.28874400	-0.06765300
H	-7.19837800	0.72723600	0.24874300
C	-2.33740800	-1.20934000	-0.79087300
H	-2.25456500	-2.29187500	-0.78689400
C	-1.10326200	-0.45244500	-1.00783800
H	-1.25096400	0.55257000	-1.39508600
H	-0.39060600	-0.98981600	-1.62949900
Se	-0.09644500	-0.22611000	0.78104900
C	1.68774700	0.14135600	0.02531000
C	2.04675900	1.48638200	-0.29132900
C	2.54202000	-0.95460500	-0.30329600
C	3.16418300	1.66918100	-1.11784200
C	3.63956500	-0.67898700	-1.13089200
C	3.92357600	0.60320900	-1.56879600
H	3.45739000	2.66273400	-1.41930700
H	4.29686000	-1.47630300	-1.44164600
H	4.76650500	0.77736600	-2.22893400
C	2.40894100	-2.41480500	0.23791500

C	1.35463600	2.77313200	0.26336100
C	3.65942400	-3.26296400	-0.10123300
H	4.58139700	-2.81196700	0.27424300
H	3.55358800	-4.24012300	0.37623700
H	3.76953300	-3.44097600	-1.17413600
C	2.17026700	4.04661900	-0.07027600
H	1.69174300	4.90025000	0.41584800
H	3.19735800	3.99164500	0.29900000
H	2.19576400	4.26068000	-1.14195900
C	-0.05226600	3.00517800	-0.33697900
H	-0.01363000	2.99400200	-1.43035300
H	-0.76443200	2.25643000	0.00105400
H	-0.42539300	3.98647800	-0.02696500
C	1.28546300	2.71679800	1.80949000
H	0.66967000	1.89550800	2.17078500
H	2.28793800	2.60973600	2.23372300
H	0.85548600	3.64739900	2.19291800
C	2.32210400	-2.40795800	1.78471800
H	3.20112400	-1.91882800	2.21429300
H	1.43159000	-1.90320300	2.15327800
H	2.29684800	-3.43786500	2.15433200
C	1.20751200	-3.17523400	-0.37270900
H	0.25572800	-2.75759200	-0.05440700
H	1.25531900	-3.16105600	-1.46589700
H	1.23719800	-4.22181500	-0.05308400

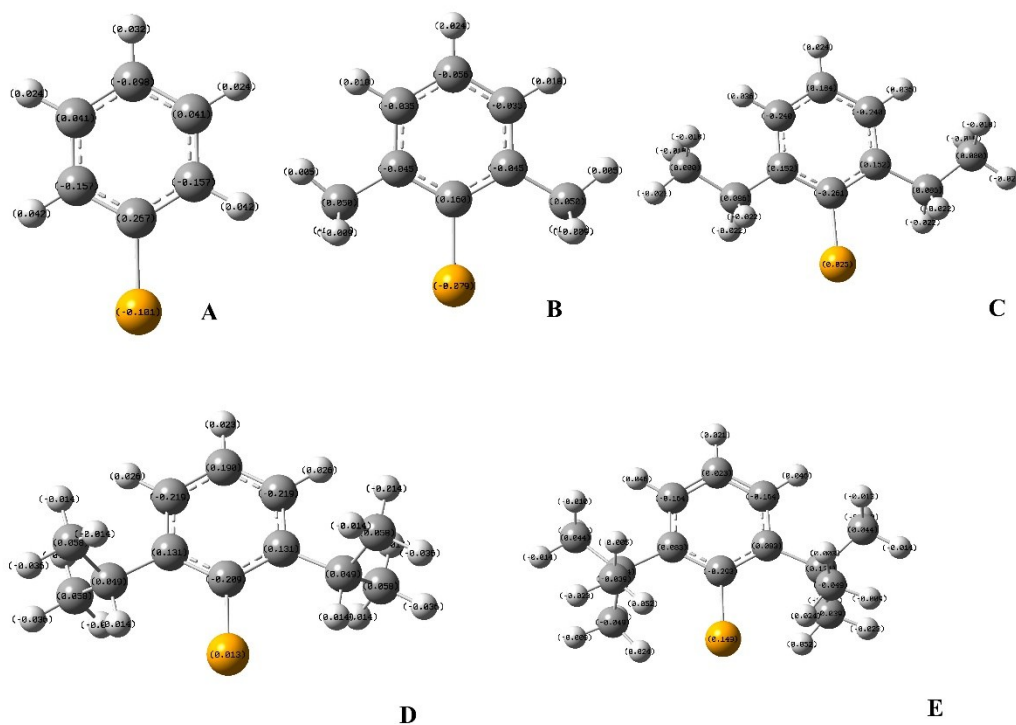


Figure 2S. Features of electron density distribution with number labelled in seleno centered radicals derived from A) DPDS; B) DmXDS; C) DEDPS; D) DiPDS; E) DtBuDPS. Calculated using the three parameter hybrid B3LYP density functional method with the extended basis set 6-311++G(d,p) implemented in the GAUSSIAN 09 package.

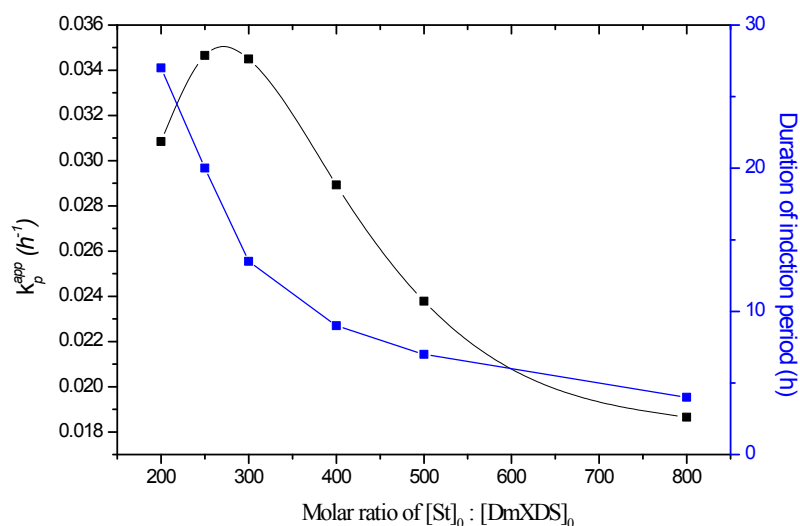


Figure 3S. The appearance polymerization rate and duration of induction period in polymerization of styrene with different DmXDS concentration under irradiation of 420 nm light.

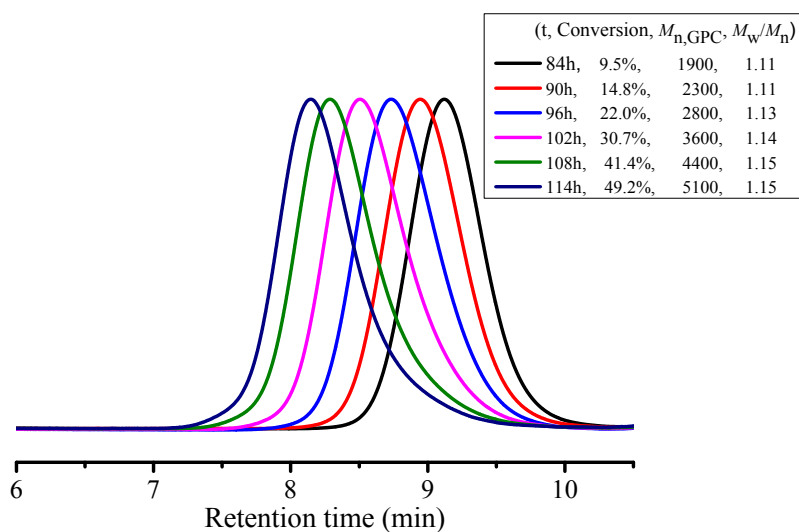


Figure 4S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 100:1$ under bulk condition at 50°C.

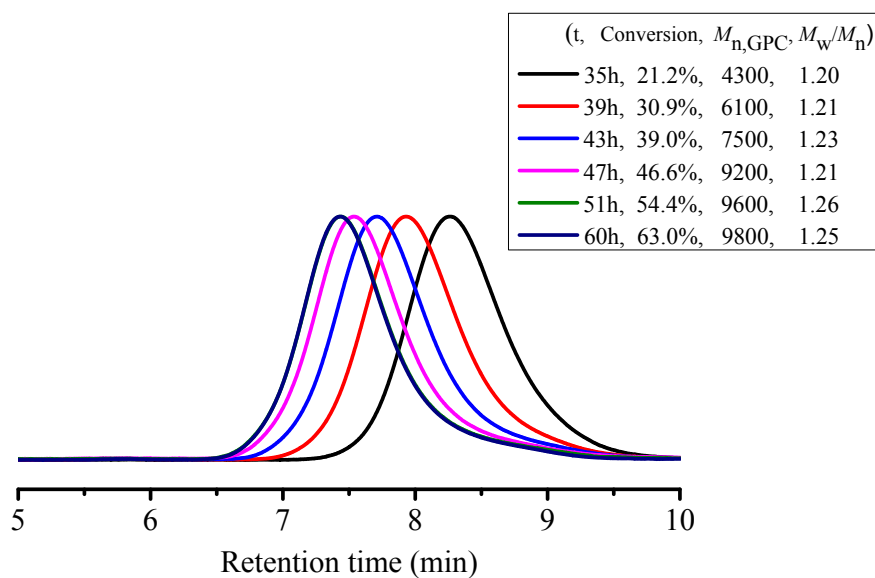


Figure 5S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 200:1$ under bulk condition at 50°C.

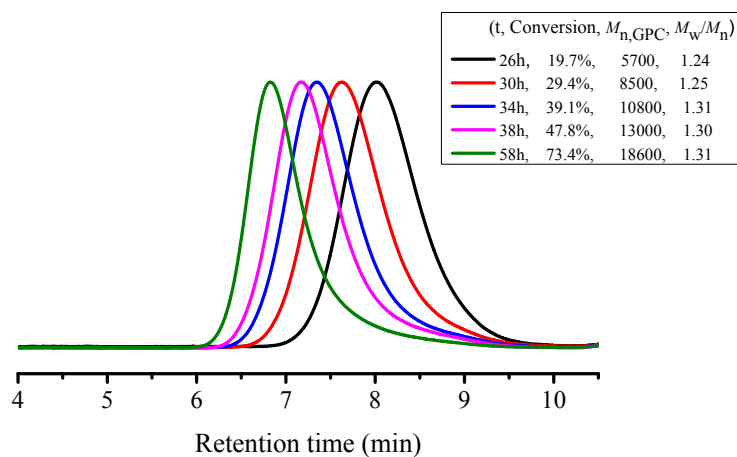


Figure 6S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 250:1$ under bulk condition at 50°C .

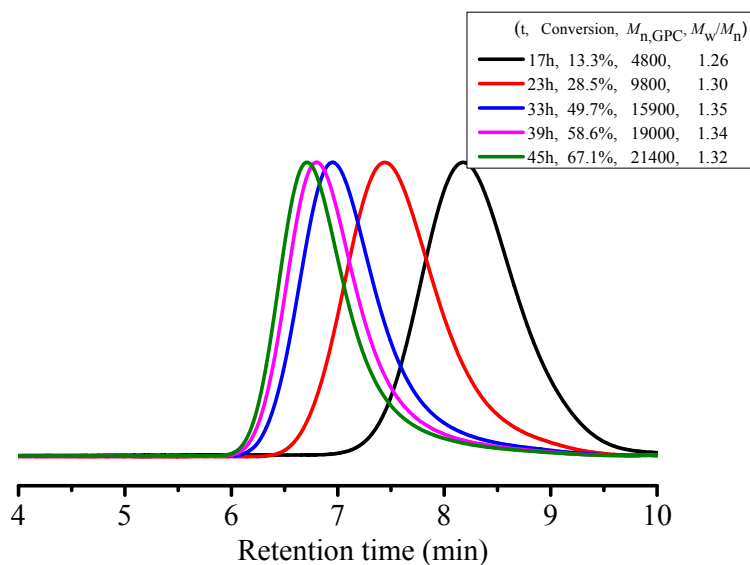


Figure 7S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 300:1$ under bulk condition at 50°C .

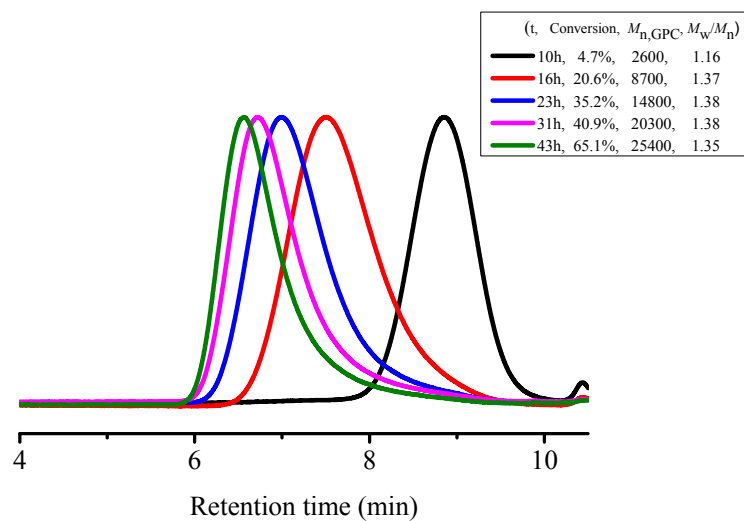


Figure 8S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 400:1$ under bulk condition at 50°C.

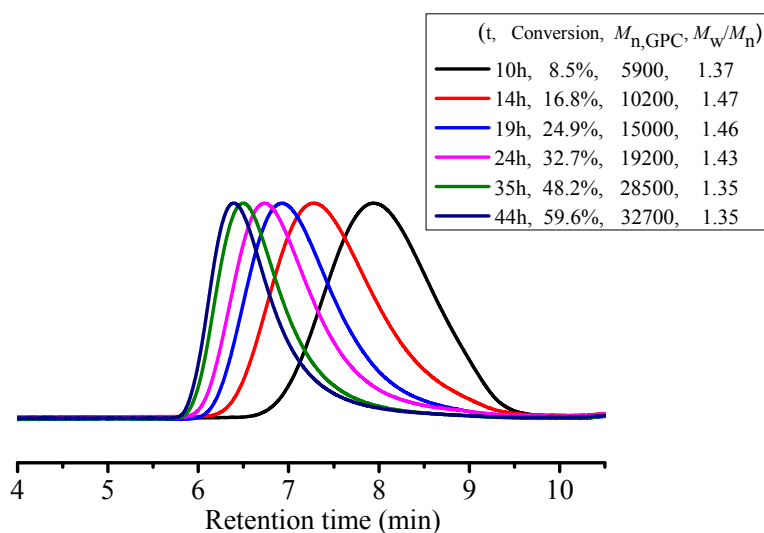


Figure 9S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 500:1$ under bulk condition at 50°C.

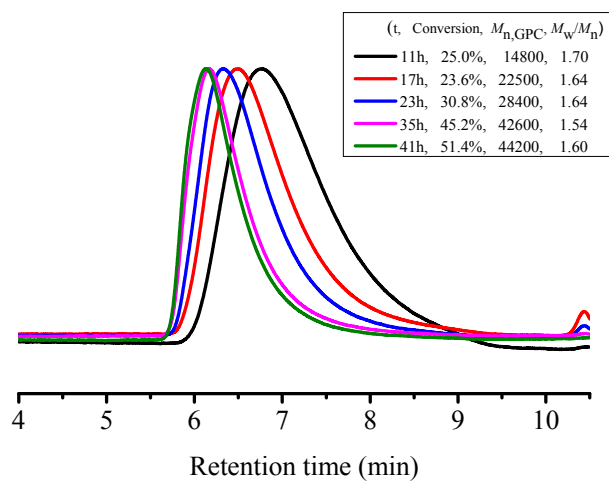


Figure 10S. Evolution of GPC traces of prepared PS-DmXDS obtained from DmXDS mediated polymerization of molar ratio $[St]_0:[DmXDS]_0 = 800:1$ under bulk condition at 50°C .