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ARTICLE

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

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The radical polymerization of styrene was investigated in the presence of five diaryl diselenide compounds with different substitution groups on benzene ring under visible light irradiation. It showed that bis(2,6-dimethylphenyl) diselenide (DmXDS) with two methyl groups on every benzene ring was the most efficient mediator for preparing polymers with predetermined molecular weight and narrow molecular weight distribution. The reasons were analyzed through quantum calculation method. The polymerization behavior of styrene in the presence of DmXDS was further investigated in depth. The results showed a typical living radical polymerization process. Polymers with high fidelity of selenide structure at both α and ω ends were verified by NMR and MALDI-TOF. Such end capped selenide groups could be transferred to terminal vinyl groups with high efficiency under oxidative condition, which offer a route to prepare "macromonomer" with narrow molecular weight distribution.

Introduction

The fast development in the field of living radical polymerization (LRP)^{1,2} or reversible-deactivation radical polymerization (RDRP)³ offered an useful technique for design and synthesis macromolecules with well-defined structures, so called macromolecule engineering.⁴ Among different LRP techniques, such as atom transfer radical polymerization (ATRP)^{5,6} and reversible addition-fragmentation chain transfer polymerization (RAFT)⁷, seleno-mediated radical polymerization (SeRP)⁸⁻¹¹ has been demonstrated as an alternative method for applicable in various monomers. Furthermore, the polymers synthesized from SeRP contained seleno moiety. Such organoselenium moiety was useful for synthetic chemistry and photochemistry. Our group has demonstrated that the terminal seleno moiety could be used to prepare diselenide linked polymer through high-efficient diselenide coupling reaction.¹² Such diselenide linked polymer showed interesting multi-responsive behaviors¹³⁻¹⁷, which has been demonstrated as the useful materials in bio-related areas by different groups.¹⁸ However, the diselenocarbonyl

compounds used in SeRP were relatively unstable, which limited its application.

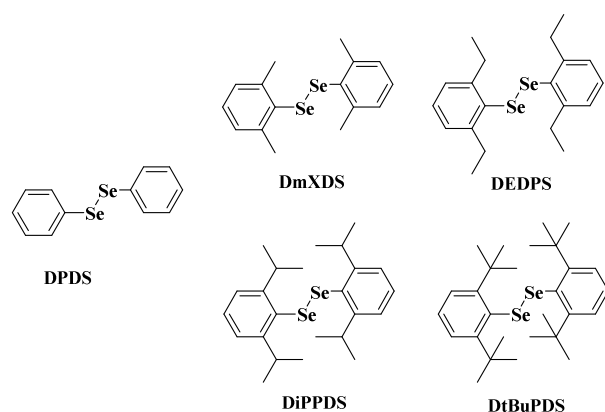
Alternatively, diaryl diselenide and selenide were representative stable organoselenium compounds, and were widely used for synthetic chemistry and photochemistry.¹⁹ The diselenide and selenide compounds have also been applied into LRP area through the iniferter mechanism.²⁰⁻³¹ Thus, polymers could be synthesized with controlled molecular weight. However, the molecular weight distribution of polymer was relative broad ($\mathcal{D} > 1.5$). Kwon et al. reported that photopolymerization in the presence of diphenyl diselenide (DPDS) afforded polystyrene carrying phenylseleno groups at both chain ends.²⁰ Rathore et al. reported the LRP of styrene by using 1-(phenylseleno)ethyl benzene/tert-butyl diphenyl (phenylseleno) silane as the mediator.²² After optimizing the selenide structure and polymerization conditions, the polymers with different topologies were realized.^{21,28,30,31} These polymers contained selenide chain ends, which could be oxidized to give the corresponding polymer with carbon-carbon double bonds.²⁰ Thus, the polymer after oxidation could be used as a macromonomer. On the other hand, diselenides with aromatic nitriles could produce electrophilic selenium species, which could be used in cationic polymerization system.³² However, the broad molecular weight distributions of obtained polymers in selenide mediated LRP was limited its further application in cases of demanding well-defined polymers.

The objective of this work was to improve the controllability of diselenide based LRP by modifying DPDS structure to synthesis polymers with controlled molecular weight along and narrow molecular weight distribution. It was

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† Electronic Supplementary Information (ESI) available: The NMR spectra and UV-vis spectra of diaryl diselenides, GPC curves of polymers, and calculation results were supplied in Supporting Information. See DOI: 10.1039/x0xx00000x

well-known that the activity of free radical was affected by the structure of



Scheme 1. The structure of diaryl diselenides with different substitution groups on the benzene ring.

substitutions through so called electronic effect and steric effect. Thus, in here we designed and synthesized different diselenides with different electronic and steric effect substitutions. The structures of diselenides were showed in Scheme 1. Due to light was demonstrated as the efficient stimuli for selenide mediated polymerization, which also was fast developed in LRP fields in recent year.³³⁻³⁸ The polymerizations of styrene in the presence of these novel diselenides under light irradiation were investigated.

Experimental

Materials

Styrene (AR, Chinasun Specialty Products Co., Ltd., China) was passed through a basic alumina column prior to use. 2-Bromo-m-xylene (99%, Adamas Reagent, China) was used as received. Other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd., China, and used as received.

Synthesis of diselenides

The bis(2,6-dimethylphenyl) diselenide (DmXDS) was synthesized according to the literature procedure.³⁹ ¹H NMR (300 MHz, CDCl₃, δ): 2.26 (s, 12H, CH₃), 7.01-6.94 (m, 4H, Ph), 7.14-7.01 (m, 2H, Ph) ppm. ¹³C NMR (300 MHz, CDCl₃, δ): 144.33, 132.51, 129.74, 127.93, 24.72 ppm. ⁷⁷Se NMR (600MHz, CDCl₃, δ) 371.60 ppm.

Preparation of 1,2-bis(2,6-diethylphenyl)diselenide (DEPDS): To a solution of 2-bromo-1,3-diethylbenzene (4.26 g, 20 mmol) in anhydrous THF (80 mL) at -78°C was added *tert*-BuLi (1.3 M pentane solution, 18.5 mL, 24 mmol) dropwise. The reaction mixture was stirred at -78°C for 1h, and the selenium powder (1.9 g, 24 mmol) was added into the reaction mixture in portions at -78°C. The reaction mixture was allowed warm to room temperature and stirred at room temperature in air for 12h. The reaction mixture was quenched by addition of aqueous HCl (30 mL) slowly at 0°C. The reaction mixture was portioned between diethyl ether (80 mL). The aqueous phase

was extracted with diethyl ether (40 mL x 2). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated. The residue was purified by silica gel flash chromatography (eluted with hexane) to give the crude product as orange solid, which was recrystallized with MeOH to give the pure product 3.75 g (89% yield) as yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 1.07 (t, 12H, CH₂CH₃), 2.66 (q, 8H, CH₂CH₃), 7.02-7.04 (m, 4H, ArH), 7.16-7.21 (m, 2H, ArH). ¹³C NMR (300 MHz, CDCl₃): δ 15.72, 30.36, 125.99, 129.71, 131.26, 149.68. ⁷⁷Se NMR (600 MHz, CDCl₃): δ 370.49 ppm.

Preparation of 1,2-bis(2,6-diisopropylphenyl) diselenide (DiPPDS) and 1,2-bis(2,6-di-tert-butylphenyl)diselenide (DtBuPDS) were similar as DEPDS. Yields of 83% and 62% were obtained respectively. DiPPDS: ¹H NMR (400 MHz, CDCl₃): δ 1.01 (d, 24H, CH(CH₃)₂), 3.47-3.61 (m, 4H), 7.04-7.06 (m, 4H), 7.20-7.25 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 23.97, 34.12, 123.49, 129.97, 130.70, 153.75 ppm. ⁷⁷Se NMR (600 MHz, CDCl₃): δ 361.55 ppm. DtBuPDS: ¹H NMR (300 MHz, C₆D₆): δ 1.28 (s, 36H, ArC(CH₃)₃), 7.41 (s, 6H, ArH). ¹³C NMR (300 MHz, C₆D₆): δ 31.10, 31.45, 33.19, 34.75, 119.34, 150.00, 150.13, 156.15 ppm.

Photo induced polymerization of Styrene

Typical procedure photo induced polymerization of styrene with diselenides was summarized as following: Mixture of styrene and diselenide was added into a dry Schlenk tube. The solution was deoxygenated by three standard freeze-pump-thaw cycles. The tube was sealed and placed under Xenon Lamp (covered with 420nm band-gap filter) at the set temperature. At timed intervals, the solutions were extracted by disposable syringe from the tube. The contents were dissolved in THF and precipitated into methanol. The polymer was obtained by filtration and dried at room temperature under vacuum to constant weight. The conversion of styrene was gravimetrically determined.

Chain Extension

The procedure of chain extension experiment was similar to the polymerization above except that the DmXDS was substituted by the polymer.

Oxidative Elimination of Terminal Group

A solution of polystyrene (0.0300 g), 30% aq hydrogen peroxide (0.1 g) in THF (1mL) was stirred for 48 hours at room temperature. After adding a little THF, the solution was dropped into methanol. Then then polymer was obtained by filtration and dried in vacuum.

Characterization

The number-average molecular weight (Mn) and molecular weight distribution (*D*) of the resulting polymers were determined by TOSOH HLC-8320 (GPC) equipped with TSK gel Multi pore HZ-N (3) 4.6×150 mm column at 40 °C. Tetrahydrofuran was served as the eluent with a flow rate of 0.35 mL/min. GPC samples were injected using a TOSOH HLC-8320 GPC plus auto sampler. The molecular weights were calibrated with PS standards. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance instrument using CDCl₃ as the solvent and

tetramethylsilane (TMS) as an internal standard. UV-vis spectra of the initiators and polymer were recorded using a Hitachi U-3900 spectrophotometer at room temperature. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Computer simulation was 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.⁴⁰

Results and discussion,

3.1. Polymerization results

Diselenide compound, DPDS, has been applied in radical polymerization of styrene by thermo or light stimuli acting as iniferter agent.²¹ The obtained polymer showed controlled molecular weight. However, the molecular weight distribution was broad, typically $D > 1.5$. In order to improve the controllability of the polymerization, novel diselenides with different substitutions on benzene ring were designed (Scheme 1). The DmXDS was synthesized according to the literature by the reaction of *p*-vinylphenylmagnesium bromide with selenium, followed by treatment with bromine. Then, the polymerization of styrene using these diselenides as the mediator was carried out at 50°C under light irradiation. The polymerization results were summarized in **Table 1**.

Initially, the polymerization of styrene was conducted under the irradiation of 365 nm light in the presence of DPDS and DmXDS at 50°C (Entries 1 and 2 in Table 1). The results indicated that the molecular weights of obtained polymer were under controlled, while the molecular weight distributions were broad ($D > 1.42$), which same as the results were showed in literatures. However, the molecular weight distribution of polymer was decreased from $D = 1.96$ in case of DPDS to $D = 1.42$ in case of DmXDS. After surveying the UV-vis spectra of these diselenides (Figure 1S in supporting information), it was found that the adsorption peak according to Se-Se bond was shifted from

Table 1 Polymerization of styrene mediated by various diselenides under UV-Vis irradiation^a

Entry	Wavelength (nm)	Diselenide	Time h	Conv.%	$M_{n,GPC}$	$M_{n,th}$	D
1	365	DPDS	16.0	17.8	5300	4100	1.96
2	365	DmXDS	46.0	42.5	8600	9200	1.42
3	420	DPDS	51.0	35.4	9100	7600	1.82
4	420	DmXDS	35.0	21.2	4300	4800	1.20
5 ^b	420	None	96.0	--	--	--	--
6 ^c	none	DmXDS	96.0	--	--	--	--
7	420	DEPDS	61.5	27.9	6800	6200	1.47
8	420	DiPDS	94.0	50.0	11900	10900	2.08
9	420	DtBuPDS	96.0	--	--	--	--

^a Xenon lamp light source using 365nm or 420 nm filter at 650 $\mu\text{W}/\text{cm}^2$ intensity.

^b The reaction in absence of DmXDS. ^c The reaction in absence of Xe irradiation.

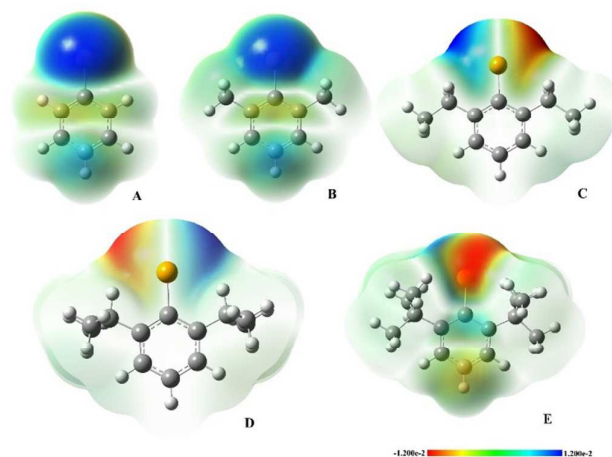


Figure 1. Features of electron density distribution in seleno centered radicals derived from A) DPDS; B) DmXDS; C) DEPDS; D) DiPDS; E) DtBuPDS. Calculated using the three parameter hybrid B3LYP density functional method with the extended basis set 6-311++G(d,p) implemented in the GAUSSIAN 09 package.

$\sim 350\text{nm}$ of DPDS to $\sim 385\text{ nm}$ of DmXDS, DEPDS, DiPDS, and DtBuPDS. Thus, in order to further improve the controllability of polymerization, the wavelength of light source was extended to 420 nm. The polymerization took place smoothly under the irradiation of 420 nm light with light intensity of 650 $\mu\text{W}/\text{cm}^2$ at 50°C (Entries 3 and 4 in Table 1). In case of DPDS, the molecular weight distribution was still showed broad, $D = 1.82$. However, in case of DmXDS, polymer with narrow molecular weight distribution ($D = 1.20$) was obtained with the monomer conversion of 21.2% after 35 hours of polymerization. The determined molecular weight of polymer was closed to theoretical value, e.g. $M_{n,GPC} = 4300\text{ g/mol}$ vs $M_{n,th} = 4800\text{ g/mol}$, assuming one polymer chain derived from per DmXDS molecule. The polymerization results showed in Entries 5 and 6 demonstrated that light irradiation and DmXDS were essential for the polymerization. DmXDS played role in the polymerization of styrene as: “initiator”, “transfer agent” and “terminator”.

After changing the mediator agent from DmXDS to DEPDS, and DiPDS, the polymerization was gradually loss of control. Polymers with broad molecular weight distributions were obtained, e.g. $D = 1.47$ of DEPDS, and $D = 2.08$ of DiPDS (Entries 7 and 8 in Table 1). The polymerization was inhibited by using DtBuPDS as the mediating agent (Entry 9 in Table 1). These results showed that the substitution groups on the benzene ring of diaryl diselenide compounds showed crucial effect on the polymerization behavior. It showed that DmXDS with two methyl groups substituted on the *o*-position of DPDS was the most effective mediator for the polymerization of styrene over other diselenides. In order to further analyze the effect of substitution on the polymerization, the electron density from total self-consistent field densities of selenide free radicals derived from these diselenides have been performed by density functional theory. The results were summarized in Figure 1. High density of free radical outer electron was located in the highest occupied molecular orbital

surrounding selenium atom. The shape of molecular orbital was similar in cases of radicals derived from DPDS and DmXDS. However, the electron density was slightly reduced in case of DmXDS due to the delocalization effect of methyl groups (Figure 2S in supporting information), which implied the more stable of such radical compared to the radical derived from DPDS. For the radicals derived from DEDPS, DiPDS, and DtBuDPS, the shapes of molecular orbital differed distinctly with those of DPDS and DmXDS. The orbitals rotated 90° in cases of radicals derived from DEDPS and DiPDS. The orbital rotated about 75° in the radical derived from DtBuDPS. The rotated molecular orbital resulted in high steric-hindrance for these radicals adding to styrene, which resulted in low polymerization rate and low efficiency of iniferter process (even no polymerization happened in case of DtBuDPS). Such hypothesis was verified by the increasing energy for the addition reaction of seleno radicals with styrene (Table 1S in supporting information). The Gibbs free energy of the reaction slightly increased from 2.95 Kcal/mol to 6.66 Kcal/mol after changing DPDS to DmXDS. While, the Gibbs free energy rapidly increased to 12.11 Kcal/mol, 11.64 Kcal/mol, and 13.72 Kcal/mol in cases of DEDPS, DiPDS, and DtBuDPS, respectively. These computer simulation combined with experimental results demonstrated that DmXDS was the optional structure for efficient control over the polymerization.

3.2. Polymerization kinetics

The polymerization behavior of styrene in the presence of DmXDS under 420 nm light irradiation was further investigated. The relationships for time- $\ln[M]_0/[M]$ and conversion- M_n and \bar{D} of the polymers were shown in Figure 2 and 3. First order polymerization kinetic in all the investigated cases well demonstrated the constant propagating radical concentration during the polymerization. Linear relationship between conversion and molecular weight of polystyrene was found (Figure 3). The value of $M_{n, GPC}$ was close to the theoretical value. The molecular weight distribution remained narrow, e.g. $\bar{D} < 1.3$, in all obtained polymers. From the above results, the polymerization was a living radical proceed. And the molecular weight distributions of polymers were narrow.

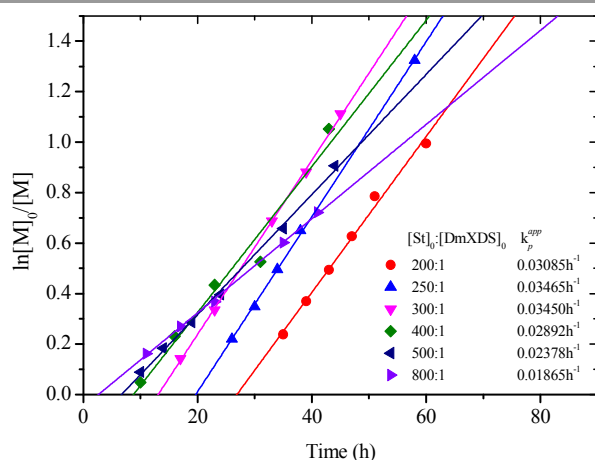


Figure 2. $\ln([M]_0/[M])$ versus time for the polymerization of styrene in the presence of the DmXDS with the different molar ratio in bulk at 50°C under the irradiation of 420 nm light with light intensity of 650 $\mu\text{W}/\text{cm}^2$.

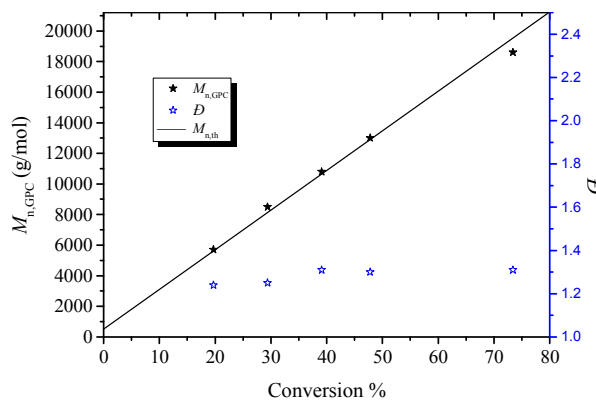


Figure 3. Dependence of M_n and \bar{D} on conversion of styrene in the presence of the DmXDS with the molar ratio $[\text{St}]_0:[\text{DmXDS}]_0 = 250:1$ in bulk at 50°C. ($M_n, \text{th} = [\text{St}]_0/[\text{Diselenide}]_0 \times \text{conversion} \times M_{\text{St}} + M_{\text{Diselenide}}$)

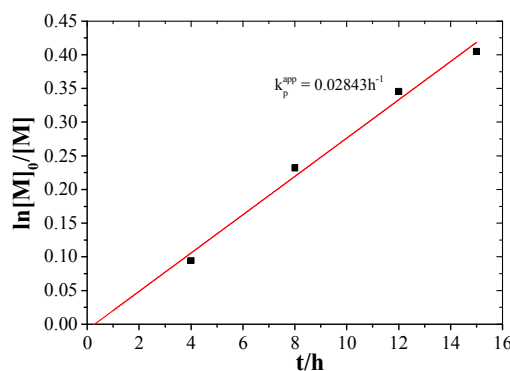


Figure 4. $\ln([M]_0/[M])$ versus time for the chain extension polymerization of styrene in bulk at 50°C under the irradiation of 420 nm light with light intensity of 650 $\mu\text{W}/\text{cm}^2$.

From Figure 2, the polymerization rate was showed complex relationships with molar ratio of $[\text{St}]_0:[\text{DmXDS}]_0$. It was increased from $k_p^{\text{app}} = 0.03085 \text{ h}^{-1}$ with $[\text{St}]_0:[\text{DmXDS}]_0 = 200:1$ to $k_p^{\text{app}} = 0.03450 \sim 0.03465 \text{ h}^{-1}$ with $[\text{St}]_0:[\text{DmXDS}]_0 = 250\text{-}300:1$. Further decreasing the concentration of DmXDS resulted in the decreasing of polymerization rate. Such results well demonstrated the multi-function, or iniferter, of DmXDS in the polymerization. The increasing concentration of DmXDS resulted in the increasing rate of initiation, which accelerated the polymerization. However, the termination reaction was increased simultaneously, which reduced the polymerization. By the combination effect of initiating and termination process, maximum polymerization rate was observed in case of $[\text{St}]_0:[\text{DmXDS}]_0 = 250\text{-}300:1$ (Figure 3S in supporting information).

It worth to further indicate that under different concentration of DmXDS, induction period from several to of

27 hours was found in Figure 2, which may due to the time consumed in pre-equilibrium between primary radicals and DmXDS. Thus, the duration of induction period was decreased with the increasing of molar ratio between monomer and

unit ($m/z = 104.06$) was found in the spectrum. The main population at $m/z = 2770.92$ was well matched with polymer with repeat unit of 20.

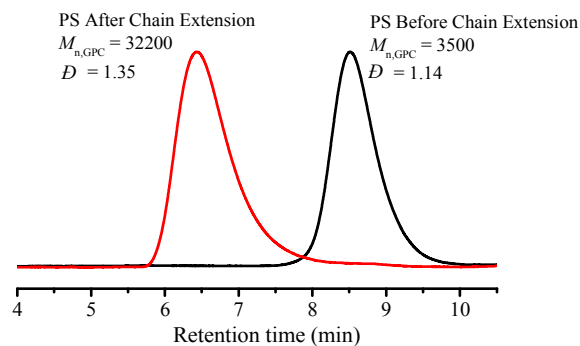


Figure 5. GPC traces of before and after chain extension using PS prepared by DmXDS as macroinitiator.

DmXDS (Figure 2S in supporting information). Lowest induction period of ~ 4 hours was observed in molar ratio of $[St]_0/[DmXDS]_0$ equaled to 800:1. Owing to the features of LRP, the resulting polymer was still active, which could be used as macroiniferter for chain extension. In such situation, the pre-equilibrium between primary radicals and DmXDS could be removed. The chain extension kinetic was showed in Figure 4. Very short induction period of ~ 10 min in chain extension verified that the induction period in presence of DmXDS was caused by the pre-equilibrium between primary radicals. Linearly increasing of $\ln([M]/[M]_0)$ with polymerization time demonstrated the constant propagating free radical concentration during the polymerization.

The GPC curves before and after the chain extension was shown in **Figure 5**. The peak of original PS was thoroughly shifted to shorter retention time range, which indicated the high activity of chain ends in the original PS. After polymerization of 35.5 h, the molecular weight of polymer increased from 3500 g/mol to 32200 g/mol with 45.6% monomer conversion. The molecular weight distribution slightly increased from 1.14 to 1.35.

3.3. Structure analysis

The structure of the polymer was characterized by 1H NMR. **Figure 6a** showed the 1H NMR spectrum for polystyrene obtained from DmXDS mediated polymerization. From **Figure 6a**, the signals at about $\delta = 3.45$ – 3.80 ppm could be assigned to the methyne protons adjacent to the selenium atom of the chain-end, which confirmed the existence of arylseleno group. The molecular weight of polymer was calculated based on 1H NMR ($M_{n,NMR} = [(I_{7.23-6.20} - 6)/5]/(I_{3.80-3.46}/1) \times 104 + 368$) = 4275 g/mol, which was very closed to 4300 ($M_{n,GPC}$) assuming per DmXDS per polymer. MALDI-TOF was further used to analysis the chain ends of obtained polymer. The mass spectrum of PS with $M_{n,GPC} = 4300$ g/mol and $D = 1.13$ was showed in **Figure 6B**. A series of population differed with mass of styrene repeat

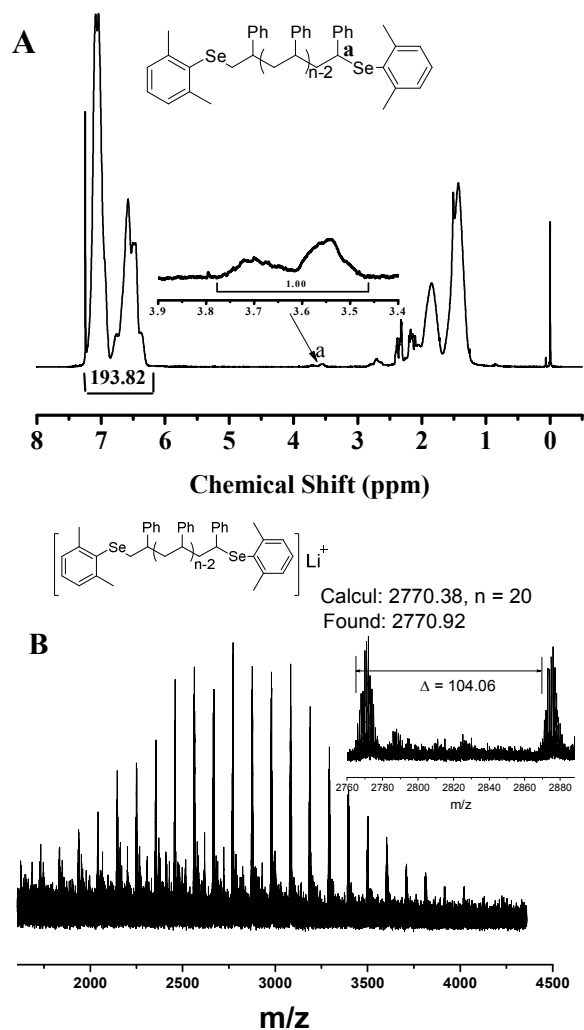
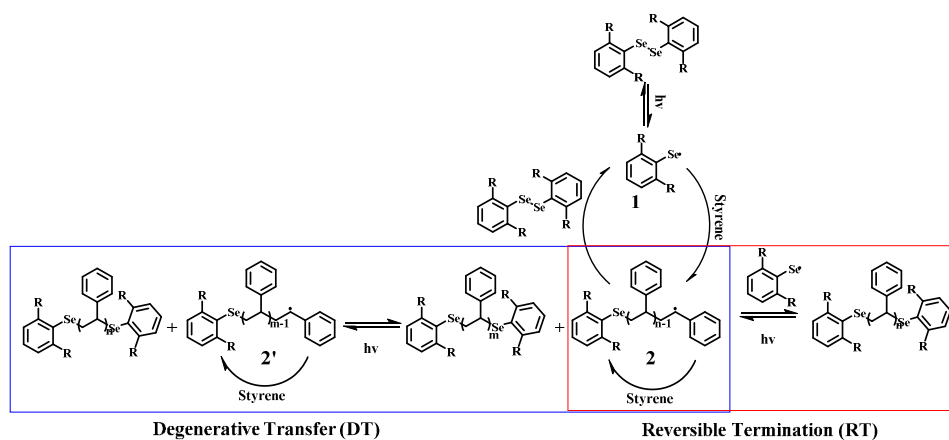


Figure 6. (A) 1H NMR spectrum of PSt ($M_{n,GPC} = 4300$ g/mol, $D = 1.13$, conversion = 21.2%) in $CDCl_3$, prepared under Xe-Lamp at $50^\circ C$. ($[St]_0/[DmXDS]_0 = 200:1$, $t = 35$ h); (B) Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of PSt ($M_{n,GPC} = 1900$ g/mol, $D = 1.11$, conversion = 9.5%, $[St]_0/[DmXDS]_0 = 100:1$, $t = 84$ h)

The selenide structure could be oxidized to the unstable selenoxide with oxidant, and then decomposed to alkene.^{20,41} Such behaviour of the obtained polymer ($M_{n,GPC} = 4300$ g/mol, $D = 1.13$) was verified by treating the polymer with hydrogen peroxide (30%). The structure of oxidized product was characterized by GPC, 1H NMR and MALDI-TOF (**Figure 7**). The GPC results showed slightly decreasing of molecular weight from 4300 g/mol to 4100 g/mol due to the elimination of selenide chain ends. The chemical shift at $\delta = 6.0$ – 6.2 ppm and 4.7 – 5.2 ppm assigned to vinyl groups was found in the 1H NMR



Scheme 2. Proposed polymerization mechanism.

spectrum of oxidized polymer. Also, the MALDI-TOF spectrum showed main population at $m/z = 4287.97$, which was well matched with the structure of di-vinyl terminated polystyrene with repeat unit number of 40. These characterization results demonstrated that the both ends of obtained polymer were terminated by diselenide moiety derived from DmXDS.

The polymerization mechanism in the presence of diselenide was proposed through modified iniferter route, which was showed in Scheme 2. Diselenide decomposed to the selenium centred radical **1** under the irradiation of light. This radical **1** added onto double bond of styrene to form the propagating radical **2** for the polymerization. Radical **2** could be transferred with diselenide. Such transfer reaction may dominate in the initial stage due to the relative high chain transfer constant of diselenide compound,²⁵ which resulted in the significant induction period. Also, radical **2** could be reversible terminated by radical **1** (RT pathway) or degenerative transferred with dormant polymer (DT pathway) to form the polymer with α, ω ditelechelic polymer. The possible fragmentation of α selenide end was excluded for the high energy demanding, which ensured the controllability of the polymerization.

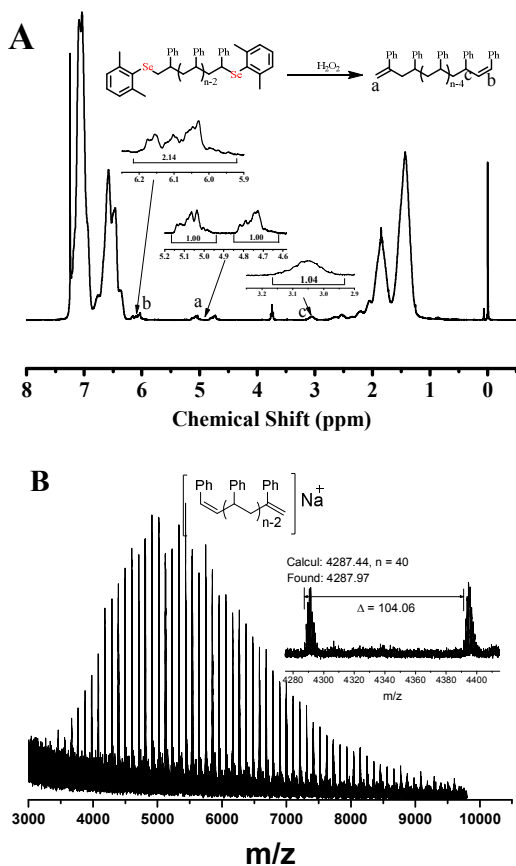


Figure 7. (a) ^1H NMR spectrum of PSt after oxidation ($M_{n,\text{GPC}} = 4700$ g/mol, $D = 1.13$) in CDCl_3 ; (b) Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of PSt after oxidation ($M_{n,\text{GPC}} = 4700$ g/mol, $D = 1.13$).

Conclusions

The effect of substitution groups in diaryl diselenide structure on the visible light induced radical polymerization behavior of styrene was investigated. The results demonstrated that DmXDS with two methyl groups on benzene ring was the most effective iniferter due to the electronic and steric effect of methyl group. The obtained polystyrene showed controlled molecular weight and narrow molecular weight distribution ($D < 1.3$). Markedly induction period was observed in the polymerization. The duration of induction period was directly related with the concentration of DmXDS, due to the time needed for establish of pre-equilibrium between primary radical with DmXDS. Such induction period could be overcome by using polystyrene as the macroinitiator to skip the pre-equilibrium process. The high end functionality of polymer in both α and ω ends with selenide structure was verified by NMR and MALDI-TOF. Such selenide end groups could be further transferred to double bond under oxidative conditions with high efficiency, to form polymerizable “macromonomer”, which was difficult to realize through normal radical polymerization. Thus, the current

results provided the alternative route to synthesize polymers with well controlled structures with selenide functional groups able for further modification.

Acknowledgements

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Notes and references

- Braunecker, W. A.; Matyjaszewski, K. *Progress in Polymer Science* **2007**, *32*, 93.
- Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.
- Jenkins, A. D.; Jones, R. G.; Moad, G. *Pure Appl Chem* **2010**, *82*, 483.
- Matyjaszewski, K. *Progress in Polymer Science* **2005**, *30*, 858.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* **1995**, *117*, 5614.
- Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
- Zeng, J.; Zhu, J.; Zhang, Z.; Pan, X.; Zhang, W.; Cheng, Z.; Zhu, X. *Journal of Polymer Science Part a-Polymer Chemistry* **2012**, *50*, 2211.
- Ma, F.; Zhu, J.; Zhang, Z.; Pan, X.; Zhou, N.; Zhu, X. *Journal of Polymer Science Part a-Polymer Chemistry* **2013**, *51*, 3159.
- Zeng, J.; Zhang, Z.; Zhu, J.; Zhou, N.; Cheng, Z.; Zhu, X. *Journal of Polymer Science Part a-Polymer Chemistry* **2013**, *51*, 2606.
- Zeng, J.; Zhu, J.; Pan, X.; Zhang, Z.; Zhou, N.; Cheng, Z.; Zhang, W.; Zhu, X. *Polymer Chemistry* **2013**, *4*, 3453.
- Gao, F.; Pan, X.; Zhu, J.; Zhang, Z.; Zhang, W.; Zhu, X. *Polymer Chemistry* **2015**, *6*, 1367.
- Ma, N.; Li, Y.; Ren, H. F.; Xu, H. P.; Li, Z. B.; Zhang, X. *Polymer Chemistry* **2010**, *1*, 1609.
- Ren, H.; Wu, Y.; Ma, N.; Xu, H.; Zhang, X. *Soft Matter* **2012**, *8*, 1460.
- Cao, W.; Zhang, X.; Miao, X.; Yang, Z.; Xu, H. *Angewandte Chemie International Edition* **2013**, *52*, 6233.
- Ren, H.; Huang, Z.; Yang, H.; Xu, H.; Zhang, X. *Chemphyschem* **2015**, *16*, 523.
- Tan, X.; Yang, L.; Huang, Z.; Yu, Y.; Wang, Z.; Zhang, X. *Polymer Chemistry* **2015**, *6*, 681.
- Xu, H.; Cao, W.; Zhang, X. *Accounts Chem Res* **2013**, *46*, 1647.
- (a) Nomoto, A.; Higuchi, Y.; Kobiki, Y.; Ogawa, A. *Mini-Rev Med Chem* **2013**, *13*, 814. (b) Yamago, S.; Nakamura, Y. *Polymer* **2013**, *54*, 981.
- Kwon, T. S.; Kumazawa, S.; Yokoi, T.; Kondo, S.; Kunisada, H.; Yuki, Y. *J Macromol Sci Pure* **1997**, *A34*, 1553.
- Kwon, T. S.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. *Polym J* **1999**, *31*, 483.
- Rathore, K.; Reddy, K. R.; Tomer, N. S.; Desai, S. M.; Singh, R. P. *J Appl Polym Sci* **2004**, *93*, 348.
- Ando, T.; Kwon, T. S.; Kitagawa, A.; Tanemura, T.; Kondo, S.; Kunisada, H.; Yuki, Y. *Macromolecular Chemistry and Physics* **1996**, *197*, 2803.
- Kwon, T. S.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. *Polym J* **1999**, *31*, 483.
- Kwon, T. S.; Kondo, S.; Kunisada, H.; Yuki, Y. *European Polymer Journal* **1999**, *35*, 727.
- Kwon, T. S.; Ochiai, H.; Kondo, S.; Takagi, K.; Kunisada, H.; Yuki, Y. *Polym J* **1999**, *31*, 411.
- KUNISADA, H.; YUKI, Y. *Polym. J* **2000**, *32*.
- Kwon, T. S.; Takagi, K.; Kunisada, H.; Yuki, Y. *Journal of Macromolecular Science, Part A* **2000**, *37*, 1461.
- Kwon, T. S.; Suzuki, K.; Takagi, K.; Kunisada, H.; Yuki, Y. *Journal of Macromolecular Science, Part A* **2001**, *38*, 591.
- Seok Kwon, T.; Takagi, K.; Kunisada, H.; Yuki, Y. *Journal of Macromolecular Science, Part A* **2002**, *39*, 991.
- Kwon, T. S.; Takagi, K.; Kunisada, H.; Yuki, Y. *European Polymer Journal* **2003**, *39*, 1437.
- Gupta, M. K.; Singh, R. P. *Macromol Symp* **2006**, *240*, 186.
- Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. *J Am Chem Soc* **2014**, *136*, 16096.
- Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. *J Am Chem Soc* **2014**, *136*, 5508.
- Dietlin, C.; Schweizer, S.; Xiao, P.; Zhang, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J.-P.; Lalevee, J. *Polymer Chemistry* **2015**.
- Zhao, Y.; Yu, M.; Zhang, S.; Wu, Z.; Liu, Y.; Peng, C.-H.; Fu, X. *Chem. Sci.* **2015**, *6*, 2979.
- Yamago, S.; Ukai, Y.; Matsumoto, A.; Nakamura, Y. *J Am Chem Soc* **2009**, *131*, 2100.
- Wenn, B.; Conradi, M.; Carreiras, A. D.; Haddleton, D. M.; Junkers, T. *Polymer Chemistry* **2014**, *5*, 3053.
- Reich, H. J.; Cohen, M. L.; Clark, P. S. In *Organic Syntheses*; John Wiley & Sons, Inc.: 2003.
- Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- Sharpless, K. B.; Young, M. W. *The Journal of Organic Chemistry* **1975**, *40*, 947.

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