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Polymer Chemistry

PAPER

Monomer Sequence Determination in the Living Anionic Copolymerization of Styrene and Asymmetric Bi-Functionalized 1,1-Diphenylethylene Derivatives†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Due to distinct steric hindrance, 1,1-diphenylethylene (DPE) and its derivatives cannot homopolymerize via living anionic polymerization and are thus advantageous for investigating the sequence structure of the corresponding copolymers. The substitution of functional groups on the benzene rings of DPE derivatives can be used to adjust the reactivity ratios for the copolymerization of styrene and the DPE derivatives. Two types of DPE derivatives, DPE-SiH/OMe and DPE-SiH/NMe_2, were designed and prepared in this work. An electron withdrawing substituent and electron donating substituent are simultaneously present at the para positions of the two phenyl rings of DPE. These derivatives were copolymerized with styrene under Schlenk conditions via living anionic polymerization. The statistical in-chain functionalized copolymers were prepared, and the corresponding average reactivity ratios were 1.42 for DPE-SiH/OMe and 1.79 for DPE-SiH/NMe_2. Additionally, a time sampling strategy under high vacuum conditions was used during the copolymerization of the two systems (styrene with DPE-SiH/OMe and styrene with DPE-SiH/NMe_2) with $[M_S]_0/[M_D]_0=4$. The kinetic parameters and statistical sequence structures were analyzed by ^1H NMR spectroscopy, SEC and MALDI-TOF MS, and the average sequential arrangements of the corresponding copolymers were determined. The critical conditions for preparing copolymers with alternating structures were determined and implemented, and the monomer unit ratios were both nearly 1:1.

Introduction

Sequence-controlled (or sequence specifically arranged) macromolecules, such as RNA and DNA have essential roles in life and conveying information.[1-3] For instance, the sequence variations of RNA and DNA underlie the diversity of life forms. Thus, the synthesis of polymers with controlled sequences has become an important topic in the field of polymer science. To achieve this objective, living controlled polymerization (LCP) has attracted considerable attention from polymer chemists. LCP has been used to prepare sequence-controlled polymers because molecular weight can be easily designed and controlled, and multiple stepwise feedings maintain the living propagation domain by domain. To control the polymeric sequential arrangement, the LCP system must fulfill certain kinetic requirements for binary copolymerization, e.g., one of the monomers may have a low tendency to homopolymerization, but both monomers highly favor cross-propagation with each other[4] (i.e., $r_1×r_2≈0$). The copolymerization systems of maleic anhydride (MAH)/styrene and maleimide (MI)/styrene are of interest because MAH and MI have strong tendencies toward cross-propagation with styrene. Lutz et al.[4,5] used the N-substituted MI/styrene copolymerization system and successfully prepared a series of sequence-controlled multiblock copolymers with ultra-precise statistical and alternating arrangement using a depending on the time multi-feed strategy (Table 1) via controlled radical chain-growth polymerizations (CRP). In addition, N-substituted MIs can graft various functional groups, which are considered information points, and introduce them into the chains of the corresponding sequence as the unsubstituted MI.[4] Thus, the corresponding functional information site can be “written” into the polymer chains accurately and sequentially.[6]

Not only CRP but also many controlled polymerization strategies are good at preparing sequence controllable polymers,[7-13] with living anionic polymerization (LAP) being the most important one among them.[14,15] Because of its steric hindrance, 1,1-diphenylethene (DPE) has an r_D (the reactivity ratio of DPE to other comonomers) of 0 when it undergoes copolymerization with the common monomer via LAP,[16] e.g., styrene,[17-19] butadiene,[20] isoprene,[21] and methacrylate.[22] Thus, DPE and its derivatives have significant advantages in the synthesis of in-chain/chain-end functionalized polymers that have sequence characteristics. First, DPE and its derivatives are

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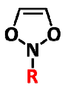
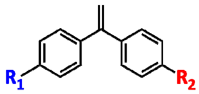
† Electronic supplementary information (ESI) available: Related characterization results that were not in the text but were referred to including ^1H NMR, ^{13}C NMR, HSQC NMR, MS, MALDI-TOF MS, DSC, some data summarized in the tables, and the graphical method for simplified calculation of r_S. See DOI: 10.1039/x0xx00000x

Table 1 The differences between the systems using controlled chain-growth polymerization methods (CRP and LAP) to synthesize the sequence-defined polymers.

Item	CRP	LAP
Copolymerization system	N-substituted Maleimide Derivatives/Styrene	1,1-Diphenylethlene Derivatives/Styrene
Functional monomer formula		
Kinetic characteristic	r_S>0, r_M>0 (r_S·r_M≈0)	r_S>0, r_D=0 (r_S·r_D=0)
Functionality	Mono-Functionalized (1)	Multi-Functionalized (≥ 1)
Sequence defined strategy	Timing multi-feed	Timing multi-feed or regulation of r_S

hardly to form dimers or trimers,[23] so they are typically used as either initiators or end-capping agents to synthesize the telechelic copolymers[15,24] and complex topology copolymers[25-35] conveniently and effectively. Furthermore, DPE derivatives can carry functional groups, and there are multiple sites in the DPE structure for polymer functionalization. The sequence-controlled functionalized polymers can be used to store or transfer information.[1,2,36] Thus, the amount of information carried by the multi-functional (either symmetric or asymmetric) DPE derivatives should be considerably greater than that carried by monofunctional comonomers. More importantly, the sequential structures of the copolymers can be adjusted by the feed ratio[37] and the reactivity ratio of styrene to DPE (r_S).[18,37,38] In that case, the feed ratio of comonomers can be designed freely. According to its definition,[39] the reactivity ratio is determined by the reaction rate constant ($k_{SS}/k_{SD}=r_S$), and k is influenced by the substituent effects.[40,41] That is, k can be adjusted by varying the type (electron withdrawing or donating) and quantity of functional groups as well as the substituted positions on the phenyl rings of DPE.[42] Therefore, the copolymerization system of styrene and DPE derivatives can easily synthesize polymers with strictly controlled sequences and arrangements. In addition, the design of DPE is the first and most important step in polymeric sequence control.

Many DPE derivatives with multiple or diverse functional groups have been synthesized and used to prepare in-chain functionalized copolymers. There are common features among these derivatives: only one functional substituent[38,43-45] or two symmetric functional substituents,[46] which only can be thought of as a "doubled single functional group", are substituted on the DPE. As noted above, DPE derivatives with functional substituent groups play important roles in polymers. Through the introduction of asymmetric multi-functional groups, DPE derivatives with multi-functional substituents based on relatively simple structures can be synthesized, and copolymers with in-chain multi-functional groups can be one-pot synthesized. The advantage of this method is that the sequence structure of binary copolymers synthesized from bi-functionalized DPE derivatives is controlled more easily and distinctly than that of the ternary copolymers synthesized from monofunctionalized DPE derivatives. Furthermore, DPE derivatives with precisely designed reactivity ratios can be obtained[42] by varying the type of functional substituents and their position on benzyl rings using the Hammett equation.[47]

Two types of asymmetric bi-functionalized DPE derivatives, DPE-SiH/OMe and DPE-SiH/NMe_2, were designed and synthesized. The same electron withdrawing substituent (dimethylsilane groups) and different electron donating substituents (methoxyl and dimethylamino group) were simultaneously substituted at the para positions of the DPE's two phenyl rings. To prepare in-chain functionalized copolymers, these DPE derivatives were copolymerized with styrene via LAP. The influence of the monomer feed ratios and reactivity ratio on the sequence structures in the corresponding copolymer chains were investigated. Additionally, the time sampling strategy under high vacuum conditions was used to investigate the precise sequential arrangements of the corresponding copolymers. In this work, sequence determination in the copolymerization of styrene and DPE derivatives was established, which can be used to synthesize and characterize the kinetics characteristic of functionalized copolymers via LAP.

Experimental

Materials

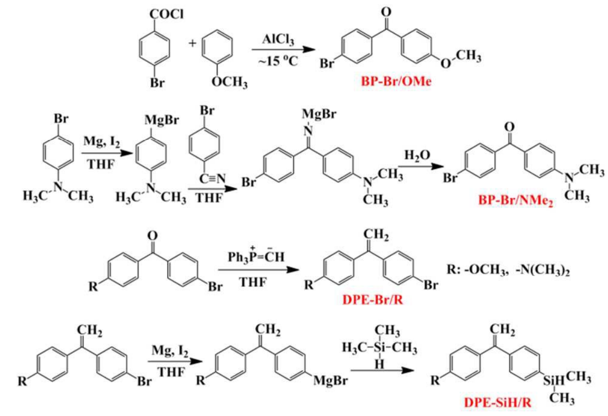
All reagents were purchased from Sinopharm Chemical Reagent Company (Shanghai, China) and used as received unless otherwise stated.

Tetrahydrofuran (THF) was dried by reflux over a Na-benzophenone complex under an argon atmosphere and then distilled. Dimethylchlorosilane (Aldrich, 98.0%) was dried by reflux over CaH_2 under an argon atmosphere and then distilled. Methyltriphenylphosphonium bromide (Energy Chemical, 98.0%), potassium tert-butoxide (Energy Chemical, 98.0%), magnesium turnings for Grignard's (J&K, 99.8%), 4-bromobenzoyl chloride (Energy Chemical, 98.0%), anisole (Energy Chemical, 99.0%), 4-bromo-N,N-dimethylaniline (Energy Chemical, 98.0%) and 4-bromobenzonitrile (Energy Chemical, 98.0%) were used as received.

The process used to purify styrene and benzene was the same as in the literature.[45] *sec*-BuLi was prepared using 2-chlorobutane and lithium metal in benzene under high vacuum conditions. The reaction procedures and apparatus used were the same as in the literature.[45] The product *sec*-BuLi was 0.38 mol/L, as determined by double titration.

Methods

^{1}H NMR (5 wt%, $CDCl_3$) spectra and ^{13}C NMR spectra were recorded on a Bruker Avance II 400M NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Size exclusion chromatographic (SEC) analyses of the copolymers were performed on a Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 mL/min in THF at 30 °C after calibration using polystyrene standard polymers. The glass



Scheme 1 Synthesis of DPE-SiH/OMe and DPE-SiH/NMe$_2$.

transition temperatures (T_g) of the polymers were measured under a nitrogen atmosphere using a TA Instruments Universal Analysis 2000 differential scanning calorimeter (DSC) from 0 to 200 °C at a heating rate of 10.0 °C /min. The sample sizes were 5 mg, and the samples were investigated under a nitrogen atmosphere. MALDI-TOF MS analysis was carried out on a Waters MALDI micro MX mass spectrometer, linear mode, DCTB, viz., 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malonitrile (Aldrich, ≥99.0% (HPLC) (Fluka)), sodium trifluoroacetate (Aldrich, ≥98.0% (HPLC) (Sigma)), and the details of the sample preparation are provided in previous studies.[48]

Synthesis of the monomers of 1-(4-methyloxyphenyl)-1’-(4-dimethylsilanephenyl)ethylene (DPE-SiH/OMe) and 1-(4-dimethylamino)-1’-(4-dimethylsilanephenyl)ethylene (DPE-SiH/NMe$_2$)

The experimental operations of synthesis precursor have been reported in the literature[49,50]. And DPE-SiH/NMe$_2$ were prepared in a similar manner as DPE-SiH/OMe[51]. The detailed synthetic process for DPE-SiH/OMe and DPE-SiH/NMe$_2$ is shown in ESI†, and the synthetic route for DPE-SiH/OMe and DPE-SiH/NMe$_2$ is shown in Scheme 1. The purities of the products were all greater than 99.5%, as identified by HPLC, and can be used for anionic polymerization.

Synthesis of the copolymers of styrene and DPE-SiH/R (P(St-co-DPE-SiH/OMe) and P(St-co-DPE-SiH/NMe$_2$)) via anionic polymerization

Copolymerization of styrene and DPE-SiH/R was carried out using sec-BuLi as the initiator in benzene under Schlenk conditions. O1 in Table 2 is taken as an example for illustration: 30 mL of benzene and 0.59 g (0.0022 mol) of DPE-SiH/OMe were added to the Schlenk ampoule under an argon atmosphere, and then, 1.9 mL (0.38 mol/L, 0.00072 mol) of *sec*-BuLi was added. The characteristic red wine color of the Si-H group substituted 1,1-diphenylalkyllithium anion appeared immediately. The solution was stirred for 15 min to ensure that the corresponding 1,1-diphenylalkyllithium was initiated sufficiently. Then, 2.5 mL (0.022 mol) of styrene was added and reacted at 25 °C for 24 h. The products were precipitated with excess methanol and subsequently dissolved in toluene, which was repeated twice until the residual DPE-SiH/OMe monomer was completely removed. If the DPE derivative was fed excessively, the unreacted DPE derivative monomer was removed by flash column chromatography (hexane/ethyl acetate 9:1 v/v). Then, the product was flushed with pure ethyl acetate, precipitated with excess methanol and dried to a constant weight in a vacuum oven.

Sequence determination for the copolymers of styrene and DPE-SiH/R by time sampling

Copolymerization of styrene and DPE-SiH/R was carried out under high vacuum conditions. The apparatus is shown in Fig. 1. **I** in Table 4 is taken as an example for illustration: It was equipped and evacuated for 4 h to high vacuum, and then, 150 mL of dry benzene was distilled into A. The apparatus was then flame sealed from the vacuum line. DPE-SiH/OMe (5.88 g, 0.022 mol) was dissolved, and 7.5 mL of *sec*-BuLi (0.38 mol/L, 0.0029 mol) was added through break seals. The colorless transparent solution immediately turned a red wine color. After 15 min, the apparatus was turned over. Styrene (10.1 mL, 0.088 mol) was added and stirred strongly in B. After 3 min, the solution was evenly poured into 12 ampoules, and approximately 10 mL of the solution was retained in B. These ampoules were immediately flame sealed from the apparatus. These reactions were allowed to react at 25 °C and were terminated with methanol every 30 min. Then, the products were precipitated in methanol. The residual monomers of DPE-SiH/OMe were removed by flash column chromatography (hexane/ethyl acetate 9:1 v/v). Then, the product was flushed with ethyl acetate, precipitated with excess methanol and dried in a vacuum oven to a constant weight.

Synthesis of alternating copolymers of styrene and DPE-SiH/R (P(St-alt-DPE-SiH/OMe) and P(St-alt-DPE-SiH/NMe$_2$))

Under Schlenk conditions, the monomer molar feed ratios shown in Table 6 were used. The reaction and post-treatment procedures are the same as those used to synthesize the copolymers of styrene and DPE-SiH/R.

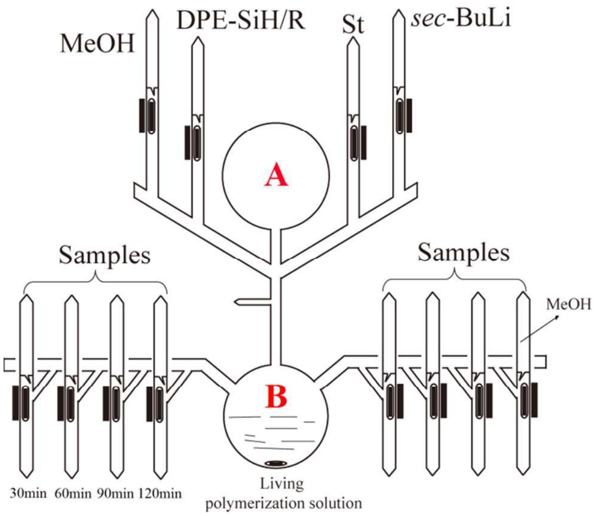


Fig. 1 Copolymerization and time sampling apparatus for styrene and DPE-SiH/R.

Results and discussion

Synthesis of P(St-co-DPE-SiH/OMe) and P(St-co-DPE-SiH/NMe$_2$)

DPE derivatives that possess abundant functional groups are often used to copolymerize via LAP, e.g., the DPE derivatives are substituted by dimethylsilane (Si-H) groups,[52-54] dimethylamine (NMe$_2$) groups,[37,38,46,55] and methoxyl (OMe) groups.[42] In addition, they are widely used for the synthesis of functionalized polymers.[45,53,56-58] However, there are few investigations into the accurate sequential arrangement for these DPE derivative units in chains.

The reactivity ratio is an essential parameter for the calculation of the copolymer composition and is also used to intuitively estimate the copolymerization tendency of two monomers according to its value. The hydrogen atoms in the two phenyl rings of DPE can be substituted by one or more functional groups; thus, the r_S of DPE derivatives can be changed by altering the substituent types. Furthermore, the copolymer structures may be controlled by changing the r_S of the DPE derivatives. For DPE derivative monomers, an electron donating substituent increases electron density on the double bond and makes an attack by the carbanionic chain-end less likely, and the effect is the opposite for an electron withdrawing substituent. DPE-NMe$_2$ (1-(4-dimethylaminophenyl)-1-phenylethylene, r_S=5.6),[38] DPE-(NMe$_2$)$_2$ (1,1-bis(4-dimethylaminophenyl)ethylene, r_S=53.7),[37] and DPE-(OMe)$_2$ (1,1-bis(4-methoxylphenyl)ethylene, k_{SD}=0.06 $L^{1/2}$×$mol^{-1/2}$×min^{-1})[42] reduced the likelihood of introduction into the polystyrene main chains due to the strong electron donating substituent and large r_S, although corresponding functional groups play significant roles in UV absorption.[59] However, on the poly(DPE)lithium (propagating DPE chain end), a strong electron withdrawing substituent (e.g., cyano group, -CN) may activate the DPE monomer but will deactivate the DPE propagating species so that k_{DS} decreased obviously and only oligomers are formed after 24h.[60,61] Therefore, a weak electron withdrawing substituent, the Si-H group, is introduced into one of the DPE phenyl rings to reduce the reactivity ratio and increase the DPE derivative contents in the corresponding copolymers. Furthermore, according to the general anionic functionalization method (GFM), which was proposed by Quirk et al.[39], Si-H functionalized polymers are sufficiently active in the post-functionalization to efficiently and conveniently link with a variety of functional moieties.[45,53] Therefore, the sequence determination in the copolymerization of styrene and DPE-SiH/OMe or DPE-SiH/NMe$_2$ is very important for subsequent investigations into the functionalization.

To investigate the possibility of introducing functional groups quantitatively into the polymer backbone - so called in-chain functionalization - the copolymerization of styrene and functionalized DPE derivatives with various comonomer feed ratios were carried out. These copolymers were collected and characterized by SEC and ^{1}H NMR, and the results are presented in Tables 1 and 2.

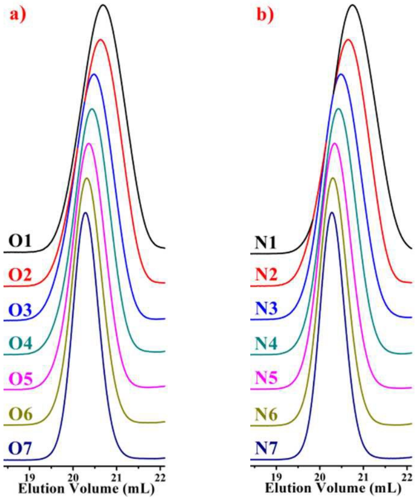


Fig. 2 SEC curves of the copolymers: a) P(St-co-DPE-SiH/OMe), O1-O7 in Table 2; b) P(St-co-DPE-SiH/NMe$_2$, N1-N7 in Table 3.

In the SEC curves of the copolymers (Fig. 2), single narrow peaks were observed in each copolymer. These peaks indicate that all of the copolymerizations in the styrene and DPE derivative system, which are initiated by alkyllithium in hydrocarbon solvents, exhibited typical characteristics of living anionic chain propagation. Furthermore, comparing O1-O7 (Table 2) and N1-N7 (Table 3), in the case of approximate molecular weights, the molecular weight distribution is narrowed after the amount of DPE derivative increased in the corresponding polymers. According to previous work,[18] the crossover propagation must occur predominantly if the reaction kinetic constant k_{DD} is sufficiently small; k_{SD}, k_{DS} and k_{SS} are quite different. The PDIs likely become wider with increasing styrene feed, because there were two living species generated during the propagation, PDIs became wider with more styrene mole fraction due to the frequent crossover of living species. In our previous work[45], when excess DPE derivatives were fed and alternating chain propagation only existed, the narrow PDIs were observed.

The ^{1}H NMR spectra of copolymers O1-O7 in Table 2 and N1-N7 in Table 3 are compared in Fig. 3, and the corresponding attributions are also listed. The characteristic vinyl (C=CH$^*_2$) peak (δ 5.3 ppm) of the DPE derivative monomer disappeared completely in the copolymers. δ 3.6-3.8 ppm can be attributed to the protons of the methoxy groups (-OCH$^*_3$) in copolymers O1-O7, and δ 2.7-3.0 ppm are the protons of the dimethylamino groups (-N(CH$^*_3$)$_2$) in copolymers N1-N7. The peaks of δ 0.2-0.4 ppm and δ 4.3-4.5 ppm can represent protons of the silylmethyl (-SiH(CH$^*_3$)$_2$) and silylhydride (-SiH*(CH$_3$)$_2$) in dimethylsilane groups, respectively. The common characteristic peaks in the ^{1}H NMR spectra of these products prove that these products are the copolymers of styrene and the corresponding DPE derivatives.

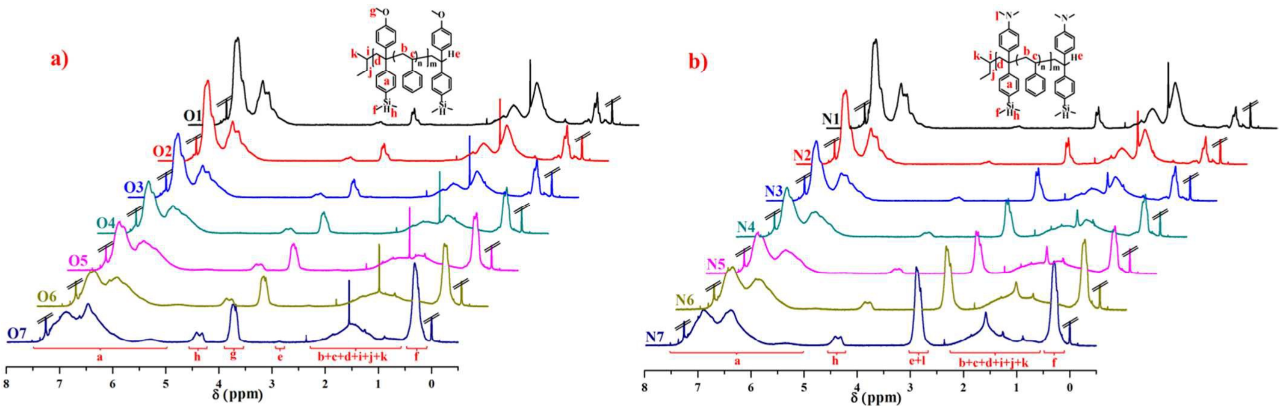


Fig. 3 SEC curves of the copolymers: a) P(St-co-DPE-SiH/OMe), O1-O7 in Table 2; b) P(St-co-DPE-SiH/NMe$_2$, N1-N7 in Table 3.

Table 2 Characteristics for the copolymerization of styrene (M_S) and DPE-SiH/OMe (M_D).

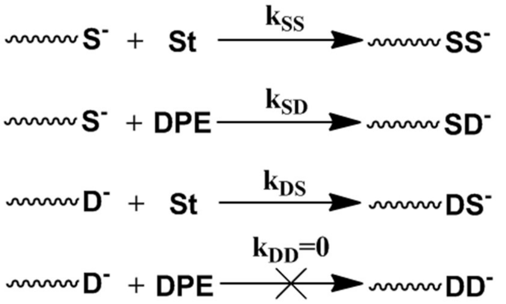
No. ^{a}	$[M_S]_0/[M_D]_0$ ^{b}	N_S/N_D ^{c}	M_n ^{d} (kg/mol)	PDI ^{d}	N_D ^{e}	T_g ^{f} (°C)	Conv.$_{DPE}$ ^{g} (%)	E_{DPE} ^{h} (%)	r_S ^{i}
O1	10.0	10.6	4.6	1.30	3.3	100	94.3	44.3	1.74
O2	8.0	8.6	4.8	1.29	4.1	104	93.0	45.1	1.72
O3	6.0	6.3	5.4	1.30	5.8	109	95.2	67.3	1.41
O4	4.0	4.2	5.9	1.24	8.3	121	95.2	>99.9	1.17
O5	3.0	3.2	6.2	1.18	10.2	125	93.8	>99.9	1.06
O6	2.0	2.2	6.9	1.16	13.7	135	90.9	>99.9	N/A
O7	1.0	1.5	7.7	1.12	18.0	146	66.7	>99.9	N/A

[a] P(St-co-DPE-SiH/OMe) (O1-O7) were synthesized at 25 °C for 24 h, $[M_S]_0/[I]$ was designed to be 30, and styrene monomer was consumed completely. [b] The monomer molar feed ratio of styrene and DPE-SiH/OMe. [c] The ratio of the two monomer units in the final copolymer, calculated from the ^{1}H NMR spectra of the copolymers using Equation 1. [d] Determined by SEC. [e] The average number of DPE in each chain, calculated from the ^{1}H NMR spectra using Equation 3. [f] Glass transition temperature, characterized by DSC. [g] The conversion ratio of DPE-SiH/OMe, calculated using Equation 4. [h] The end-capped ratio of DPE-SiH/OMe, calculated using Equation 5. [i] The reactivity ratio of styrene to DPE-SiH/OMe, calculated from the ^{1}H NMR spectra of the copolymers using Equation 8.

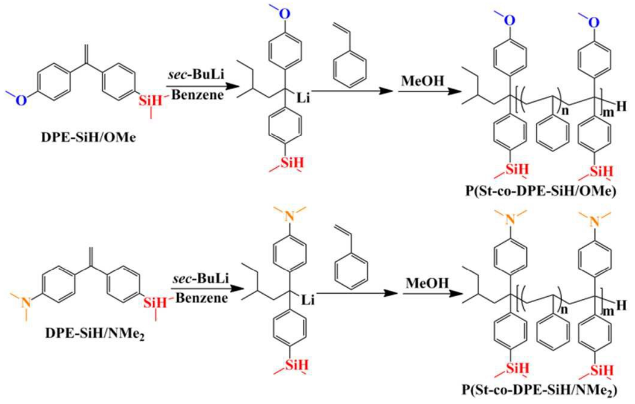
Table 3 Characteristics for the copolymerization of styrene (M_S) and DPE-SiH/NMe$_2$ (M_D).

No. ^{a}	$[M_S]_0/[M_D]_0$ ^{b}	N_S/N_D ^{c}	M_n ^{d} (kg/mol)	PDI ^{d}	N_D ^{e}	T_g ^{f} (°C)	Conv.$_{DPE}$ ^{g} (%)	E_{DPE} ^{h} (%)	r_S ^{i}
N1	10.0	11.1	4.5	1.32	3.1	102	90.1	N/A	2.06
N2	8.0	9.0	4.7	1.32	3.8	107	88.9	N/A	2.00
N3	6.0	6.6	5.4	1.30	5.5	113	90.9	N/A	1.68
N4	4.0	4.4	5.9	1.22	7.9	127	90.9	N/A	1.40
N5	3.0	3.5	6.5	1.17	10.0	133	85.7	N/A	N/A
N6	2.0	2.5	7.5	1.13	13.8	145	80.0	N/A	N/A
N7	1.0	1.8	7.9	1.10	16.8	157	55.6	N/A	N/A

[a] P(St-co-DPE-SiH/NMe$_2$) (N1-N7) were synthesized at 25 °C for 24 h, $[M_S]_0/[I]$ was designed to be 30, and styrene monomer was consumed completely. [b] The monomer molar feed ratio of styrene and DPE-SiH/NMe$_2$. [c] The ratio of the two monomer units in the final copolymer, calculated from the ^{1}H NMR spectra of the copolymers using Equation 2. [d] Determined by SEC. [e] The average number of DPE in each chain, calculated from the ^{1}H NMR spectra using Equation 3. [f] Glass transition temperature, characterized by DSC. [g] The conversion ratio of DPE-SiH/NMe$_2$, calculated using Equation 4. [h] The end-capped ratio of DPE-SiH/NMe$_2$, could not be calculated from the corresponding ^{1}H NMR spectra. [i] The reactivity ratio of styrene to DPE-SiH/NMe$_2$, calculated from the ^{1}H NMR spectra of the copolymers using Equation 8.



Scheme 2 Typical copolymerization propagation of styrene and DPE in LAP.



Scheme 3 Copolymerization of styrene with DPE-SiH/OMe and styrene with DPE-SiH/NMe$_2$.

The ratio of the two monomer units in the final copolymer, N_S/N_D, was determined using ^{1}H NMR as well as Equation 1 for P(St-co-DPE-SiH/OMe) and Equation 2 for P(St-co-DPE-SiH/(NMe)$_2$) in Table 1S in ESI†. The average number of DPE derivative units in each polymer chain was calculated using Equation 3 in Table 1S. The value of the conversion rate (Conv.$_{DPE}$) for DPE derivative can be obtained from ^{1}H NMR using Equation 4 in Table 1S, and the value of the end-capped ratio (E_{DPE}) for DPE-SiH/OMe can be obtained from δ 2.87 ppm in the corresponding ^{1}H NMR spectra using Equation 5 in Table 1S. The end-capped ratio of DPE-SiH/NMe$_2$ cannot be calculated from the corresponding ^{1}H NMR spectra due to the interference of the dimethylamino groups in the range of δ 2.7-3.0 ppm.

The typical copolymerization propagation of styrene and DPE in LAP could be described by these four equations[38] and shown in Scheme 2. And the copolymeric procedure of styrene and DPE-SiH/R was shown in Scheme 3, although the resulting copolymers are drawn with terminal DPE units, this is not the situation in all cases - see tables 1 and 2.

Here, the styrene monomer is consumed completely, and the reaction rate constant, k_{DD}, is zero due to steric hindrance[18,38]. Unless under extreme conditions, i.e., an excess feed ratio of DPE ($[M_D]/[I]=11$) and extended reaction times (8-24 h) in chain initiation.[62] However, the oligomer of DPE is not observed in chain propagation under more DPE feed ratio conditions.[23] Therefore, the monomer reactivity ratio for DPE to styrene is 0 ($r_D=k_{DD}/k_{DS}=0$).[38]

The residual concentration of DPE derivative monomer ($[M_D]$) can be calculated from the ^{1}H NMR spectrum of each copolymer using Equation 6 in Table 1S in ESI†. In addition, for $[M_S]$, Equation 7 in Table 1S was used. Generally, the calculation of reactivity ratios is carried out a low monomer conversion, e.g., 10%. However, when DPE was used as a comonomer, $k_{DD}=0$, the calculation was different from typical conditions. Yuki et al.[18] deduced Equation 8 on Table 1S as an empirical formula for the calculation of the reactivity ratio, which is applicable to $[M_S]=0$ and $[M_D]\neq0$ when the reactions have gone to completion.[15,18] According to Equation 8, a graphical method for the simplified calculation of r_S was deduced and is shown in ESI†.

The reactivity ratio of styrene to the DPE derivatives, r_S, generally obeyed the Hammett relationship and is described by Equation 9 in Table 1S in ESI†.[38] Here, r_S^0 is the reactivity ratio of the copolymerization for styrene with 1,1-diphenylethyene and $r_S^0=0.45$ in benzene.[63] The value of σ for the para-dimethylamino substituent is -0.50,[37,38] σ for the para-methoxy substituent is -0.27,[64] and σ for the para-dimethylsilane substituent is +0.04,[64] and ρ=+1.8[37,38] is substituted into Equation 9. The theoretical values of $r_{S\text{-}O}^{th}=1.17$, and $r_{S\text{-}N}^{th}=3.03$ are obtained.

The two monomer conversions and end-capped efficiency of DPE derivatives are important indexes for copolymers to investigate the kinetic characteristics of the copolymerization. In other studies[31,32,56], it has been shown that the end-capping efficiency of DPE can reach 100% when there is a sufficient excess of DPE. However, the total conversion of the DPE monomers in this study does not reach 100% and needs to be discussed for two general cases: 1. where the monomer feed ratio has DPE is in molar excess of styrene, the conversion of DPE cannot reach 100%. DPE cannot homopolymerise and even a perfect alternating copolymer cannot consume an excess of DPE. 2. where the mole ratio of styrene is in excess of DPE, the conversion of DPE is influenced by the reactivity ratio, r_S: if $r_S\leq1$, the R_D (the chain propagation rate for DPE) was higher than R_S and the conversion can theoretically reach 100%; if $r_S>1$, the R_D was lower than R_S which led to the existence of residual DPE monomers in the solution while styrene was consumed completely, and the total conversion of DPE cannot reach 100%. In previous reports, with the r_S increasing the conversion of DPE decreased, e. g., DPE conversion=35-48% for DPE-NMe ($r_S=5.6$)[38], and conversion = 8-10% for DPE-NMe$_2$ ($r_S=53.7$)[37]. Therefore, in this case, the actual amount of DPE participating in the polymerization cannot be equal to its corresponding feed. And although chain propagations are all initiated by 1,1-diphenylalkyllithiums, the values of the reactivity ratios fluctuate within a small range. Thus, the arithmetic average values of the monomer reactivity ratio for styrene to DPE-SiH/OMe ($r_{S\text{-}O}$) and for styrene to DPE-SiH/NMe$_2$ ($r_{S\text{-}N}$) are 1.42 and 1.79, respectively. When two functional groups substituted (e.g., SiH/OMe and SiH/NMe$_2$) in different phenyls of DPE unit, one of the phenyl rings was distorted by an angle of 37° from co-planarity with the other phenyl ring and the diphenylmethyl carbon.[58,65] Therefore, the total substituent constant σ of bi-substituted DPE derivatives is not strictly equal to $\sigma_{SiH}+\sigma_{OMe}$ or $\sigma_{SiH}+\sigma_{NMe2}$ in theory, and these values are slightly different from the theoretical values of $r_{S\text{-}O}^{th}=1.17$ and $r_{S\text{-}N}^{th}=3.03$.

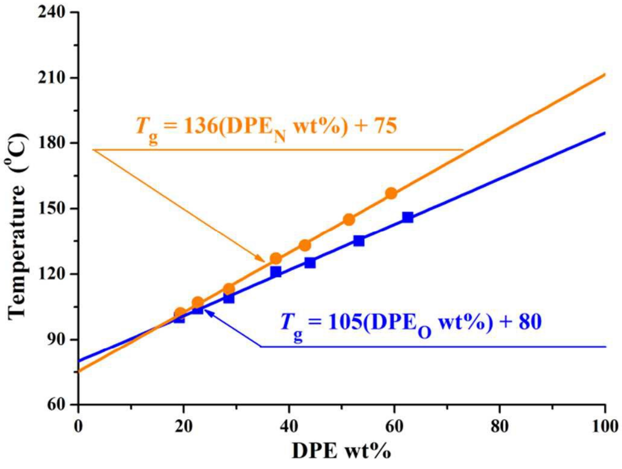


Fig. 4 Graph showing the correlation between T_g and DPE$_R$ wt% for copolymers of DPE-SiH/R and styrene.

According to previous studies,[37] the amount of DPE and its derivatives in the copolymers can affect the glass transition temperatures (T_g) of the copolymers. Thus, the thermal properties of these copolymers were investigated using differential scanning calorimetry (DSC). The relevant data are listed in Tables 1 and 2, and the corresponding DSC curves are shown in Fig. 4S in ESI†. Only one glass transition temperature could be observed for each copolymer. The molar feed ratio of styrene to initiator ($[M_S]_0/[I]$) was designed as 30 in O1-O7 and N1-N7, and styrene monomers were consumed completely when the copolymerization finished. Therefore, the thermal properties of the copolymers are influenced by the relative amount of DPE units. To quantify this influence, the T_g values for the copolymers are plotted as functions of the weight percent of DPE units in them (DPE derivative wt%) in Fig. 4. The correlations between T_g and the compositions of P(St-co-DPE-SiH/OMe) and P(St-co-DPE-SiH/NMe$_2$) can be fit using Equations i and ii, and R^2>99.8%:

$$T_{g,O}\ (°C)=105(DPE_O\ wt\%)+80 \qquad \textbf{(i)}$$

$$T_{g,N}\ (°C)=136(DPE_N\ wt\%)+75 \qquad \textbf{(ii)}$$

The slopes of Equations i and ii may be different because of the variation in the molecular weights and sequential arrangements in different segment of chains[15,66] and, perhaps, the relative contributions of the two different DPE monomers to the intramolecular forces. Furthermore, the intercepts of Equations i and ii were less than 100 in the literatures[15,66,67], which may also result from the smaller molecular weight, particularly in the number of styrene units. The T_g of polystyrene (M_n=3,000 and M_n=3,500) are estimated using Equation 10[38] in Table 1S in ESI†: $T_{g,PS3000}$=72 °C and $T_{g,PS3500}$=76 °C are obtained, which correspond well with Equations i and ii when "DPE derivative wt%=0".

Although homopolymers of DPE-SiH/OMe and DPE-SiH/NMe$_2$ do not exist, their glass transition temperature could be extrapolated from Equations i and ii with "DPE derivative wt%=100". In addition, the extrapolation values of the glass transition temperature for homopolymers of DPE-SiH/OMe and for homopolymers of DPE-SiH/NMe$_2$ are $T_{g\text{-}O}^{ex}$=185 °C and $T_{g\text{-}N}^{ex}$=211 °C, respectively. $T_{g\text{-}O}^{ex}$ and $T_{g\text{-}N}^{ex}$ are slightly lower than the previously reported extrapolated values of the glass transition temperature for homopolymers of 1,1-diphenylethene 209 °C,[15] 219 °C,[66] and 226 °C.[67] The differences might result from the lower molecular weights in this work.

As discussed above, two types of DPE derivatives with asymmetric bi-functional groups were copolymerized with styrene, and a series of copolymers were obtained successfully. The copolymerization characteristics and reactivity ratios r_S were investigated. By studying the relationship between the molar feed ratio and the molar ratio in the copolymers of the two monomers, the corresponding linear empirical formulas were obtained. It was easy and convenient to control the functional group content in the copolymer by adjusting the molecular weight and molar feed ratios of the styrene and the corresponding DPE derivatives. Based on these factors, the sequential arrangements were further investigated.

Sequence determination in the copolymerization of styrene and DPE derivatives

By controlling the functionalized monomer sequence, the functional groups can be introduced quantitatively at relatively precise positions in the copolymers. Thus, artificial and sequence-controlled functionalized polymers will provide functions similar to biological molecules in nature, such as organocatalysis, selective transport, signal transduction and data storage,[1,3,68] and the polymers can bring excellent performances and expand applications for in-chain functionalized copolymers. Lutz et al.[5,69,70] performed many studies on sequence-controlled polymers in LCP. Although it has been rarely investigated, with few existing studies on sequence determination in chain propagation,[15,45,60] LAP has the intrinsic advantages that it can introduce functional groups quantitatively at relatively accurate positions in polymers and precisely control the

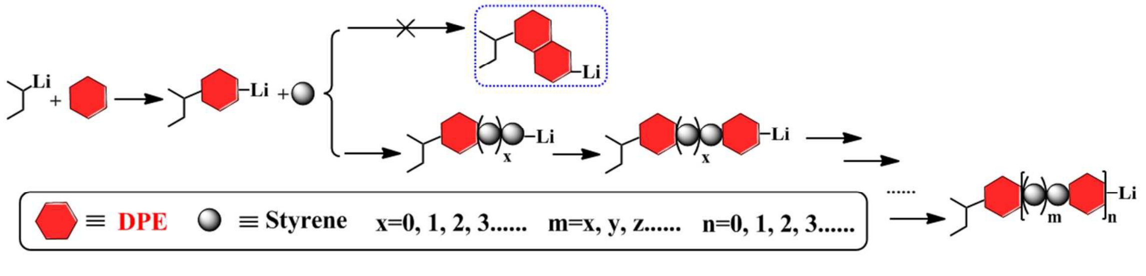


Fig. 5 Chain propagation process for the copolymerization of styrene and DPE.

Table 4. Time sampling results for the copolymerization of styrene (M_S) and DPE-SiH/R (M_D).

Sample [a]	Time (min)	M_n [b] (kg/mol)	PDI [b]	N_S/N_D [c]	N_S [d]	Conv.$_{St}$ [e] (%)	N_D [f]	Conv.$_{DPE}$ [g] (%)	E_{DPE} [h] (%)
I	30	2.9	1.10	4.5	17.4	48.5	3.9	43.3	96.1
	60	4.4	1.13	4.4	26.3	73.3	6.0	66.7	92.3
	90	5.0	1.15	4.4	29.9	83.3	6.8	75.6	96.8
	120	5.3	1.15	4.3	31.6	88.0	7.3	81.1	94.1
	180	5.7	1.16	4.2	33.6	93.6	8.0	88.9	>99.9
	300	6.0	1.18	4.2	35.5	98.9	8.4	93.3	99.3
	420	6.1	1.18	4.2	35.9	100.0	8.6	95.6	>99.9
II	30	2.1	1.19	4.9	12.7	36.2	2.6	29.5	N/A
	60	2.8	1.23	4.6	16.6	47.3	3.6	40.9	N/A
	90	3.5	1.24	4.5	20.7	59.0	4.6	52.3	N/A
	120	4.2	1.24	4.4	24.7	70.4	5.6	63.6	N/A
	180	4.9	1.25	4.4	28.8	82.1	6.6	75.0	N/A
	300	5.9	1.25	4.3	34.5	98.3	8.0	90.9	N/A
	420	6.0	1.25	4.3	35.1	100.0	8.2	93.2	N/A

[a] P(St-co-DPE-SiH/OMe) (**I**), P(St-co-DPE-SiH/NMe$_2$) (**II**) are copolymerized at 25 °C, the monomer molar feed ratio $[M_S]_0/[M_D]_0=4$, and $[M_S]_0/[I]$ is set to 30. [b] Determined by SEC. [c] The ratio of the two monomer units in the final copolymer, calculated from the ^{1}H NMR spectra of the copolymers using Equations 1 and 2. [d] The average number of styrene units in each chain is calculated from the ^{1}H NMR spectra. [e] The relative conversion of styrene. [f] The average number of DPE in each chain is calculated from the ^{1}H NMR spectra using Equation 3. [g] The relative conversion of DPE. [h] The end-capped ratio of DPE-SiH/OMe, is calculated using Equation 5. The end-capped ratio of DPE-SiH/NMe$_2$, could not be calculated from the corresponding ^{1}H NMR spectra.

polymer structure (see Fig. 5). Furthermore, the progress of LAP can be detected conveniently and accurately by various characterization methods. [15,19,48,71] Thus, based on the previous discussions, it is necessary to investigate the in-chain sequential arrangements of the two monomers, to determine the values of "m" and "n" in Fig. 5, to obtain the sequence structure of corresponding copolymers, and to establish a method to determine the sequential arrangements in LAP.

Time sampling was utilized and performed under high vacuum conditions to determine the average sequential arrangements of the copolymers. In a short time interval, time sampling is equivalent to taking a differential of the copolymerization. The reaction equipment is shown in Fig. 1. The copolymerization of styrene with DPE-SiH/OMe (**I**) and styrene with DPE-SiH/NMe$_2$ (**II**) were the research objects. According to the data in Tables 1 and 2, the molar feed ratios were set to 4 because the conversions and end-capped ratios of these two types of DPE derivatives are the largest and the reactivity ratios are nearly the smallest in this case. $[M_S]_0/[I]$ was set to 30, and all samples were taken every 30 min. The total reaction times were 7 h. The composition of each monomer in the copolymers was investigated using ^{1}H NMR. The results are listed in Table 4, and the SEC curves are shown in Fig. 6 (the full results are shown in Table 2S in ESI†).

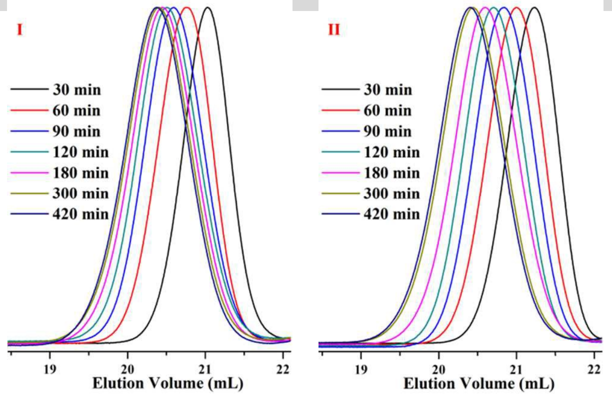


Fig. 6 SEC curves of time sampling for copolymer **I** and **II**.

The chain propagations finished in 6 h, but the DPE derivative monomers did not react completely. The conversions for two types of DPE derivatives did not reach 100%, even if the reaction time was prolonged to 24 h (Tables 1 and 2), for the reasons mentioned previously.

The kinetics equations of the corresponding copolymerization could be deduced from the results in Table 4. Copolymerization I was taken as an example for kinetic study. The consumption rates of styrene and DPE-SiH/OMe monomers were obtained using Equations 11 and 12[39] in Table 1S in ESI†. In these equations, the apparent kinetic constant is shown to be "1/2" order with respect to the "living species concentration" because poly(styryl)lithium ([S$^-$

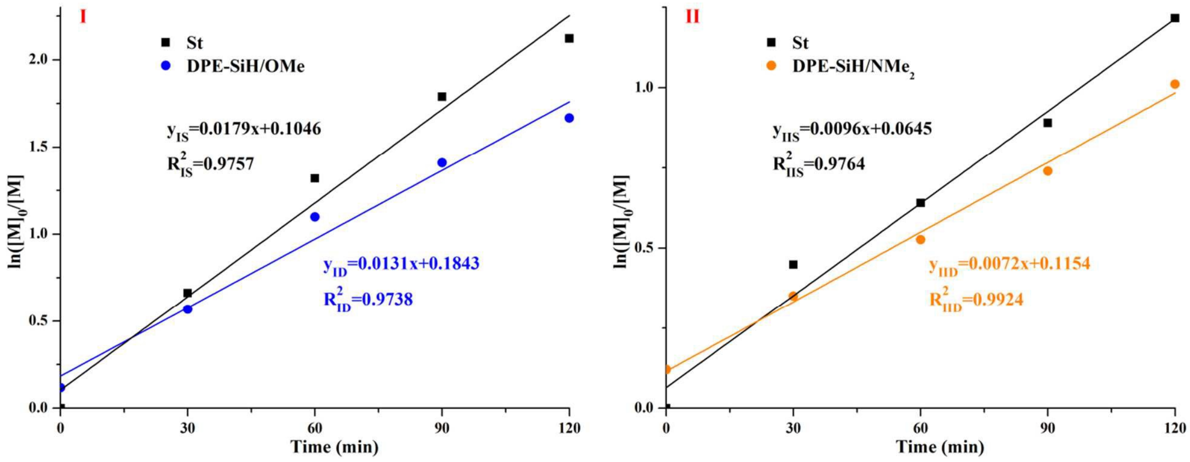


Fig.7 Apparent kinetic curves for copolymerizations **I** and **II** and the dependence of ln([M]$_0$/[M]) on the reaction time.

Table 5. Kinetic results for copolymerization **I** and **II**.

Sample	r_S [a]	$[I]_0$ (mol/L)	k_{SS} ($L^{1/2}$×$mol^{-1/2}$×min^{-1})	k_{SD} ($L^{-1/2}$×$mol^{-1/2}$×min^{-1})	k_{DS} ($L^{-1/2}$×$mol^{-1/2}$×min^{-1})
I	1.17	0.0154	0.5536	0.4732	0.0210
II	1.29	0.0156	0.3344	0.2592	0.0020

[a] The reactivity ratio of styrene to the corresponding DPE derivatives, calculated from the ^{1}H NMR spectra of the copolymers using Equation 8.

]) and poly(DPE-SiH/OMe)lithium ([D$^-$]) predominantly formed dimers in hydrocarbon solution.[39,63] [S$^-$] and [D$^-$] are instantaneous values following the corresponding time in the copolymerization of styrene and DPE, which cannot be obtained directly from Table 4. However, [D$^-$]/[I] is equal to the value of the end-capped ratio (E_{DPE}) of DPE-SiH/OMe in each copolymer, which can be calculated from the corresponding ^{1}H NMR spectrum of each sample using Equation 5 and is listed in Table 4. E_{DPE} of DPE-SiH/OMe is approximately 95% after 120 min when the propagation reaction is initiated. Thus, [D$^-$]/[I] can be used as a constant and substituted into the equations for simplified calculation. Subsequently, [S$^-$] was calculated from Equation 13 in Table 1S in ESI†, where [I] is the concentration of the initiator, which remains constant in LAP.

The linear apparent kinetic curves for the propagation of copolymerizations **I** and **II** were obtained from ln([M]$_0$/[M]) vs. time (in Fig. 7). The apparent kinetic constants of **I**, k_{IS} and k_{ID} were obtained from the slopes of the corresponding straight lines in Fig. 7I, as well as the apparent kinetic constants of **II**, k_{IIS} and k_{IID} were obtained from the slopes of corresponding straight lines in Fig. 7II using Equations 14 and 15 in Table 1S in ESI†. The corresponding reaction kinetic constants, k_{SS}, k_{SD}, k_{DS}, and k_{DD} for the copolymerizations I and II are expressed in Equations 11 and 12[39] in Table 1S, respectively.

According to the actual concentration of the initiator in system **I**, [I]=15/6100/0.16 g/(g/mol)/L=0.0154 mol/L, $k_{ISS}/k_{ISD}=r_{IS}=1.17$, $k_{ISS}×(0.05[I])^{1/2}+k_{IDS}×(0.95[I])^{1/2}=k_{IS}=0.0179$ $L^{1/2}$×$mol^{-1/2}$×min^{-1}, $k_{ID}=k_{ISD}[S^-]^{1/2}+k_{IDD}[D^-]^{1/2}$, and $k_{IDD}=0$ (DPE cannot be homopolymerized). Thus, $k_{ISD}=k_{ID}/[S^-]^{1/2}=k_{ID}/(0.05[I])^{1/2}=0.4732$ $L^{1/2}$×$mol^{-1/2}$×min^{-1}, $k_{ISS}=r_{IS}×k_{ISD}=0.5536$ $L^{1/2}$×$mol^{-1/2}$×min^{-1}, and $k_{IDS}=0.0210$ $L^{1/2}$×$mol^{-1/2}$×min^{-1}. In addition, the kinetics parameters for copolymerization of **II** were calculated using the same method. The end-capped ratio of DPE-SiH/NMe$_2$ cannot be obtained from the corresponding ^{1}H NMR spectra directly; thus, the value is taken to be approximately 95% according to the copolymerization of **I**. All of the results are shown in Table 5. The value of k_{ISS} corresponded well with the previous reports,[72] which obtained a value of $k_{SS}=0.5630$ $L^{1/2}$×$mol^{-1/2}$×min^{-1}, in homopolystyrene at 25 °C in benzene. Szwarc et al.[63] reported the anionic copolymerization of styrene and 1,1-diphenylethylene (DPE) by poly(styryl)lithium in benzene. The value of k_{SS} is $0.94×10^{-2}$ $L^{1/2}$×$mol^{-1/2}$×s^{-1} (0.5640 $L^{1/2}$×$mol^{-1/2}$×min^{-1}), $k_{DS}=7.7×10^{-4}$ $L^{1/2}$×$mol^{-1/2}$×s^{-1} (0.0462 $L^{1/2}$×$mol^{-1/2}$×min^{-1}), and $k_{SD}=2.1×10^{-2}$ $L^{1/2}$×$mol^{-1/2}$×s^{-1} (1.2600 $L^{1/2}$×$mol^{-1/2}$×min^{-1}). The above data are in good agreement with our measured data from the experiment, indicating that this simplified approach is feasible.

According to the results in Table 5, $k_{IDS}=0.0210$ $L^{1/2}$×$mol^{-1/2}$×min^{-1} for DPE-SiH/OMe and $k_{IIDS}=0.0020$ $L^{1/2}$×$mol^{-1/2}$×min^{-1} for DPE-SiH/NMe$_2$. Both of these values are smaller by one or more orders of magnitude than the corresponding k_{SS} and k_{SD}. Thus, crossover propagation is clearly present in the copolymerization, and k_{DS} is the rate-determining step. Due to the strong electronegativity of the hydrogen atoms in the double bond, the electrophilic addition of poly(styryl)lithium is retarded in DPE derivatives containing electron donating substituents in the phenyl rings (DPE-D),[42,73] and the opposite effect is observed in DPE derivatives containing electron withdrawing substituents (DPE-W). For the electron donating substituents, such as -OCH$_3$ and -N(CH$_3$)$_2$, a greater substituent constant σ in the same condition results in a smaller kinetic constant k_{SD} and a greater influence of the crossover propagation. According to Tables 1, 2, 4 and 5, the reaction kinetic

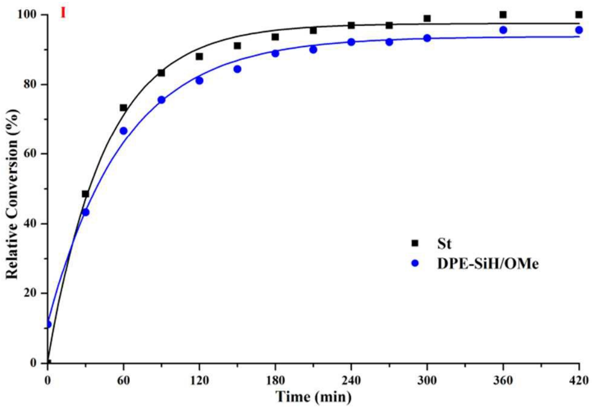


Fig. 8 Correlation between the conversion and time for copolymerizations **I** and **II**.

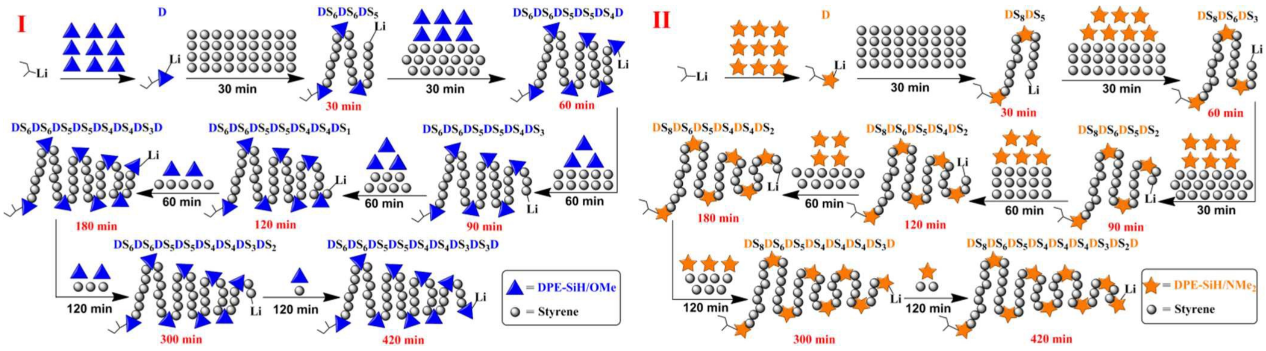


Fig.9 Steps in the chain propagation of copolymers **I** and **II**.

constants influence the reactivity ratios ($r_{IS}<r_{IIS}$) and the structures of the copolymers -- PDI of copolymer **II** is greater than **I**. In addition, for the same DPE derivative, the crossover propagations increase frequently as the feed amount of DPE increases, and their effects are gradually weakened.

According to the results in Table 4, the corresponding curves of conversion vs. time are plotted in Fig. 8.

The relatively precise position information of the DPE derivative units in corresponding copolymer chains was obtained by calculating the molecular weights and compositions of the samples, which were time-sampled from copolymerizations **I** and **II**, and integrating the inference of the polymerization. Then, the statistical sequence of the corresponding copolymer was determined. According to the results in Table 4, the average sequence structures for copolymers **I** and **II** are described and plotted in Fig. 9. A comparison of **I** and **II** in Fig. 9 indicated that the arrangements of copolymer sequences changed gradually and notably. At the beginning of propagation, polystyrene blocks are clearly observed within 30 min in the copolymers because there are many styrene monomers in the solution and $k_{SS}>k_{SD}>k_{DS}$. Then, most of the styrene monomers have been consumed by 120 min after propagation and are introduced into the fronts of the chains because the chain propagation rate, R_S, is always greater than R_D. The propagations are still proceeding, but the speeds are decreased. After 180 min, these propagations are both nearly finished, and the relative quantities of DPE derivatives in the copolymers are larger. In addition, N_S/N_D decreases rapidly and approaches the feed ratios ($[M_S]_0/[M_D]_0=4$). This phenomenon is more notable when the reactivity ratio is greater (such as **II**). This result indicates that the sequential arrangement in the copolymer is influenced by the reactivity ratio. In addition, sequence-controlled copolymers can be obtained through the design of reactivity ratio, and the r_S is adjusted by the choice of substituent groups (electron withdrawing or donating) and the substituent site on the phenyl groups.

To verify the sequence determination, every sampling point of sample **I** for 150 min from copolymer **I** was characterized by MALDI-TOF MS for accurate molecular weights, and the corresponding curves are listed in Fig.s 5Sa-e in ESI†. The peak with the highest intensity (marked with red stars) in each curve gradually moved to the high-molecular-weight region due to the introduction of monomer units into the polymer chains. After the propagation proceeded for 30 min, the red star was calculated to be $S_{15}D_2$ (*m/z*=2,174.6, exact mass=57.07+1.01+22.99+104.06×15+268.13×2=2,178.2 g/mol), which means that in the first 30 min, 15 styrene monomers and 1 DPE-SiH/OMe monomer participated in the propagation. After 60 min, the red star was calculated to be $S_{20}D_3$ (*m/z*=2,959.3, exact mass=57.07+1.01+22.99+104.06×20+268.13×3=2,966.7 g/mol), which means that in the second 30 min, 7 styrene monomers and 1 DPE-SiH/OMe monomer were introduced into the living chain. Then, the propagation gradually slowed down. The red star was calculated as $S_{24}D_4$ (*m/z*=3,634.2, exact

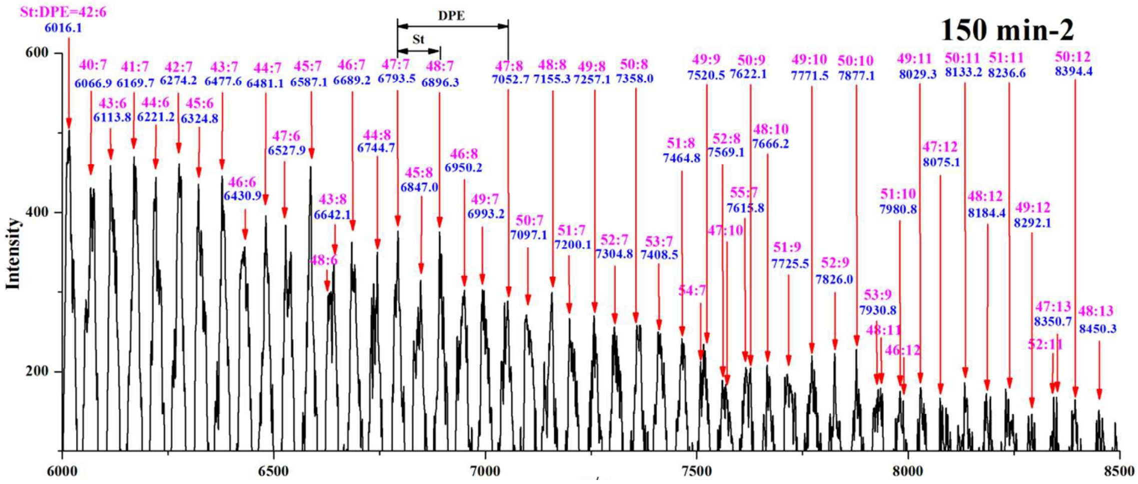


Fig.10 MALDI TOF mass spectrum for copolymer **I** (part in *m/z*=6,000-8,500 g/mol) from the 150 min sample.

mass=57.07+1.01+22.99+104.06×24+268.13×4=3,651.0 g/mol) after 150 min. As the propagation continued, the peak profiles in the MALDI-TOF MS spectra simultaneously became gradually wider. The widening trend corresponds with the data calculated from ^{1}H NMR and characterized using SEC. The living anionic copolymerization, time sampling, characterization method, and calculation method for the proportion of these two monomer units is credible, and a method for the sequence determination of copolymers of styrene and DPE derivatives has been successfully constructed.

Synthesis of approximately alternating copolymer of styrene and DPE-SiH/R

Yuki et al.[18] reported that in a system for the anionic copolymerization of styrene and 1,1-diphenylethlene, $k_{SS}/k_{SD}=r_S<1$ and $k_{DD}=0$. An essentially alternating copolymerization proceeded if the molar feed ratio of the monomers was $[M_S]_0/[M_D]_0<1/(1-r_S)$. Hutchings et al.[15] prepared alternating sequence copolymers of styrene and 1,1-diphenylethlene and characterized them using MALDI TOF MS. Li et al.[51] prepared alternating sequence copolymers of styrene and dimethyl(4-(1-phenylvinyl)phenyl)silane (DPE-SiH). All of the above studies used either DPE or DPE derivatives with electron withdrawing groups, DPE-W, and they obeyed this polymerization regularity ($r_S<1$). Alternating sequences in copolymers composed of styrene and DPE derivatives with strong electron donating groups, DPE-D, are difficult to obtain. Quirk et al.[38] used 1-(4-dimethylarninophenyl)-1-phenylethylene (DPE-NMe_2), and Li et al.[37] used 1,1-bis(4-dimethylaminophenyl)ethylene (DPE-$(NMe_2)_2$) to copolymerize with styrene; however, both of their N_D/N_S were over 4.38,[38] and their r_S values were 5.6 and 53.4, respectively. Therefore, the alternating copolymerization of styrene and DPE with weak electron donating groups must be further investigated.

The range of *m/z*=6,000-8,500 in Fig. 5Se in ESI† is magnified, and the spectrum is shown in Fig. 10. Each relatively strong peak among their adjacent peaks has been assigned and marked on the upper portion of the figure. As an example, *m/z*=6,016.1 was calculated to be $S_{42}D_6$ (exact mass=57.07+1.01+22.99+104.06×42+268.13×6=6,060.3 g/mol), and *m/z*=8,394.4 was calculated to be $S_{50}D_{12}$ (exact mass=57.07+1.01+22.99+104.06×50+268.13×12=8,501.6 g/mol). The content of styrene in the lower-molecular-weight chains (Mn≈6,000 g/mol), decreased gradually compared with that in the higher-molecular-weight chains (Mn≈8,400 g/mol), ($S_{42}D_6 \rightarrow S_{48}D_{13}$). In contrast, the content of DPE-SiH/OMe increased. Because the reactivity ratio remained unchanged in the same system, the decrease in N_S/N_D occurred due to the decreased molar concentration ratio of the free monomer ($[M_S]/[M_D]$) in the system. During propagation, $[M_S]$ decreased faster than $[M_D]$ ($k_{SS}>k_{SD}$). Therefore, when the propagation approached the end, $[M_S]$ was far less than $[M_D]$. In that case, the chain propagation rate, R_S, was less than R_D (Equations 11 and 12 in Table 1S). The DPE derivative contents increased greatly in the copolymers. These results demonstrate that $[M_S]/[M_D]$ is the key to control the amount of DPE units in the copolymers. If $[M_S]/[M_D]$ is quantified and controlled in the feed, the functionalized copolymers with higher contents of DPE derivatives and even alternating copolymers can be obtained.

Following the reaction kinetics, the critical condition of $R_S=R_D$ should be meet to obtain the copolymer with alternating sequences. That is, Equations 14 and 15 in Table 1S on the right-hand sides are equal, and Equation iii is obtained:

$$\frac{[M_D]^C}{[M_S]^C}=\left(\frac{[M_S]^C}{[M_D]^C}\right)^{-1}=\frac{k_{SS}}{k_{SD}}+\frac{k_{DS}}{k_{SD}}\left(\frac{[D^-]}{[S^-]}\right)^{\frac{1}{2}}=r_S+\frac{k_{DS}}{k_{SD}}\left(\frac{[D^-]}{[S^-]}\right)^{\frac{1}{2}} \qquad \textbf{(iii)}$$

where $[M_D]^C/[M_S]^C$ is the critical ratio. If $[M_D]/[M_S]$ is always greater than this ratio during propagation, the alternating copolymer can be obtained. $[M_D]/[M_S]$ has an upper limit: Dimers of DPE will be produced if there is excess DPE monomer in the system.[62] For the copolymerizations of I and II, $[M_D]/[M_S]$ gradually increases over time in a sealed system. Therefore, to obtain the alternating copolymer of styrene and DPE-D, the molar feed ratio ($[M_D]_0/[M_S]_0$) should be larger than the critical feed ratio ($[M_D]_0^C/[M_S]_0^C$), i.e., Equation iv should be satisfied.

$$\frac{[M_D]_0}{[M_S]_0}=\left(\frac{[M_S]_0}{[M_D]_0}\right)^{-1}>\frac{[M_D]_0^C}{[M_S]_0^C}=r_S+\frac{k_{DS}}{k_{SD}}\left(\frac{[D^-]}{[S^-]}\right)^{\frac{1}{2}} \qquad \textbf{(iv)}$$

The corresponding reactivity ratios and kinetic parameters of I and II in Table 6 were substituted into Equation iv, and the critical

Table 6. Monomer feed ratio, composition, and glass transition temperature data for the copolymers of styrene (M_S) with DPE-SiH/R (M_D).

NO. [a]	DPE-SiH/R	$[M_S]_0/[M_D]_0$ [b]	N_S/N_D [c]	M_n [d] (kg/mol)	PDI [d]	N_D [e]	T_g [f] (°C)	T_g^{th} [g] (°C)
PS	----	----	----	5.1	1.04	----	86	----
AO1	OMe	0.50	1.11	4.7	1.10	12.0	141	199
AO2	OMe	0.33	1.04	4.4	1.11	11.5	139	191
AO3	OMe	0.25	1.03	4.4	1.11	11.5	138	187
AN1	NMe_2	0.50	1.24	4.3	1.10	10.3	149	237
AN2	NMe_2	0.33	1.14	3.8	1.11	9.3	148	230
AN3	NMe_2	0.25	1.06	4.0	1.09	10.0	149	221

[a] Polystyrene (PS), P(St-alt-DPE-SiH/OMe) (AO1-AO3), and P(St-alt-DPE-SiH/NMe_2) (AN1-AN3) were polymerized at 25 °C for 24 h, $[M_S]_0/[I]$ of PS was set to 50, any other $[M_S]_0/[I]$ were set to 15, and styrene monomer was consumed completely. [b] The monomer molar feed ratio of styrene and the corresponding DPE derivative. [c] The ratio of the two monomer units in the final copolymer, calculated from the ^{1}H NMR spectra of the copolymers using Equations 1 and 2. [d] Determined by SEC. [e] The average number of DPE in each chain, calculated from the ^{1}H NMR spectra using Equation 3. [f] The glass transition temperature, characterized by DSC. [g] The theoretical value of the glass transition temperature for homopolymers of the corresponding DPE derivatives, calculated using Equation 16.

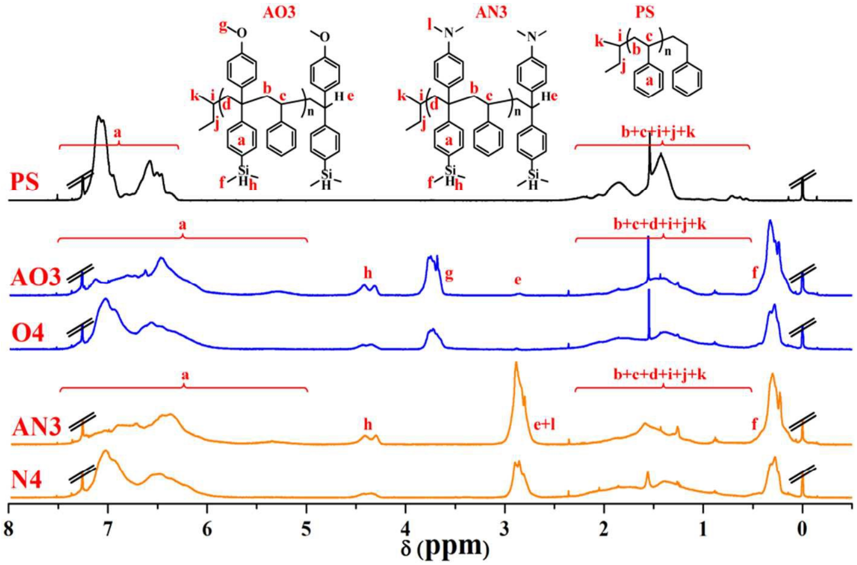


Fig. 11 ^{1}H NMR spectra (in $CDCl_3$) of homopolystyrene (PS), copolymers of styrene with DPE-SiH/OMe (AO3, O4) and copolymers of styrene with DPE-SiH/NMe_2 (AN3, N4).

feed ratios, $[M_O]_0^C/[M_S]_0^C$=1.36 ($[M_S]_0^C/[M_O]_0^C$=0.74) and $[M_N]_0^C/[M_S]_0^C$=1.32 ($[M_S]_0^C/[M_N]_0^C$=0.76), were obtained.

To prove this inference, the copolymerizations of styrene with DPE-SiH/OMe and styrene with DPE-SiH/NMe_2 were carried out for feed ratios ($[M_S]_0/[M_D]_0$) of 0.5, 0.33 and 0.25. The molecular weight of styrene in the copolymer ($M_{n,S}$) for each sample was set to 1,500 ($[M_S]_0/[I]$=15). After removing the residual DPE derivatives monomers, all the copolymers were obtained. The corresponding parameters were characterized using SEC and ^{1}H NMR and are listed in Table 6. The results show that the styrene monomers were consumed completely at 24 h; narrow PDIs were achieved because crossover propagation occurred frequently.

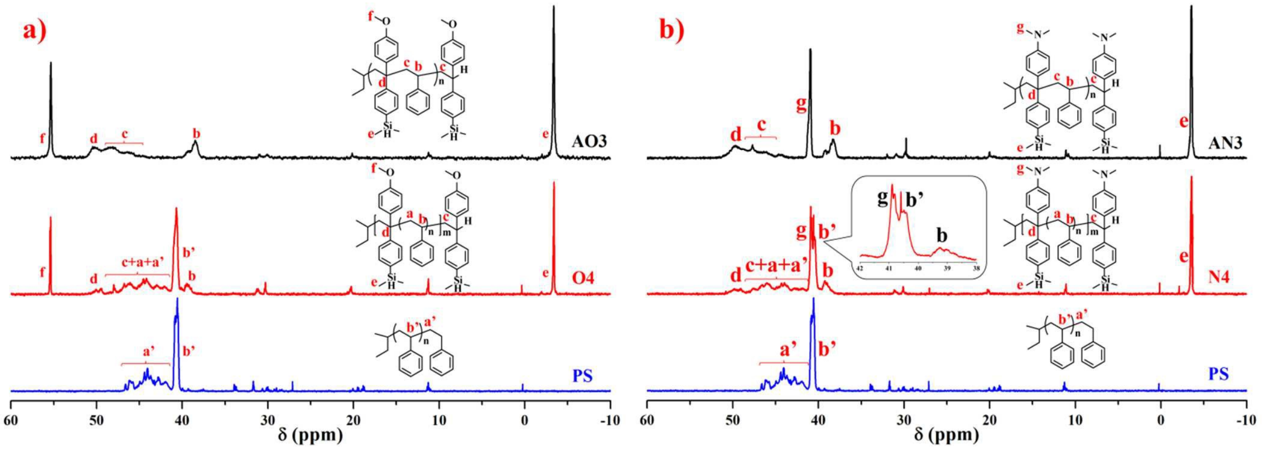


Fig. 12 ^{13}C NMR spectra (in $CDCl_3$) of homopolystyrene (PS), copolymers of styrene with DPE-SiH/OMe (a) and copolymers of styrene with DPE-SiH/NMe_2 (b).

To compare the ratio changes of the corresponding peaks for AO3 (N_S/N_D=1.03), AN3 (N_S/N_D=1.06), and PS in Table 6, O4 (N_S/N_D=4.2) in Table 2, and N4 (N_S/N_D=4.4) in Table 3, the ^{1}H NMR spectra are shown in Fig. 11. In addition, the ratio details of the corresponding peaks are shown in Fig. 7S in ESI†. After the feed amount was increased gradually, the DPE derivative contents in the copolymer increased continuously but slowly. The DPE derivative contents in copolymers AO2 and AO3 are similar, which means that the DPE-D contents in the copolymers have already reached their limits from reducing the feed ratio. If $[M_S]_0/[M_D]_0$ is reduced continuously, the risk of producing dimers of DPE derivatives during initiation will increase greatly.[62] The ^{13}C NMR spectra of AO3, AN3, PS, O4 and N4 are shown in Fig. 12. The styrene-styrene random block characteristic peak at δ 41.5-46.5 ppm is smaller in O4 and N4, and it is completely absent in AO3 and AN3. There is good agreement between the critical ratio and the experiment results, and approximately alternating copolymers were prepared.

Approximately alternating copolymers of AO3 and AN3 were characterized by MALDI-TOF MS, and their corresponding spectra are shown in Fig. 13 and Fig. 6S in ESI†. The main peak in each figure was calculated. For example, in Fig. 13, *m/z*=3,547.7173 was calculated to be $S_{10}D_9$ (exact mass=57.07+1.01+22.99+104.06×10+268.13×9=3,534.84), and *m/z*=3,919.5303 was calculated to be $S_{11}D_{10}$ (exact mass=57.07+1.01+22.99+104.06×11+268.13×9=3,907.03). Three components (black, n-1:n; red, n:n; blue, n:n-1) reflect the alternating polymerization between styrene and DPE-SiH/OMe. The MALDI data shown in Fig. 6S in ESI† indicates several distributions

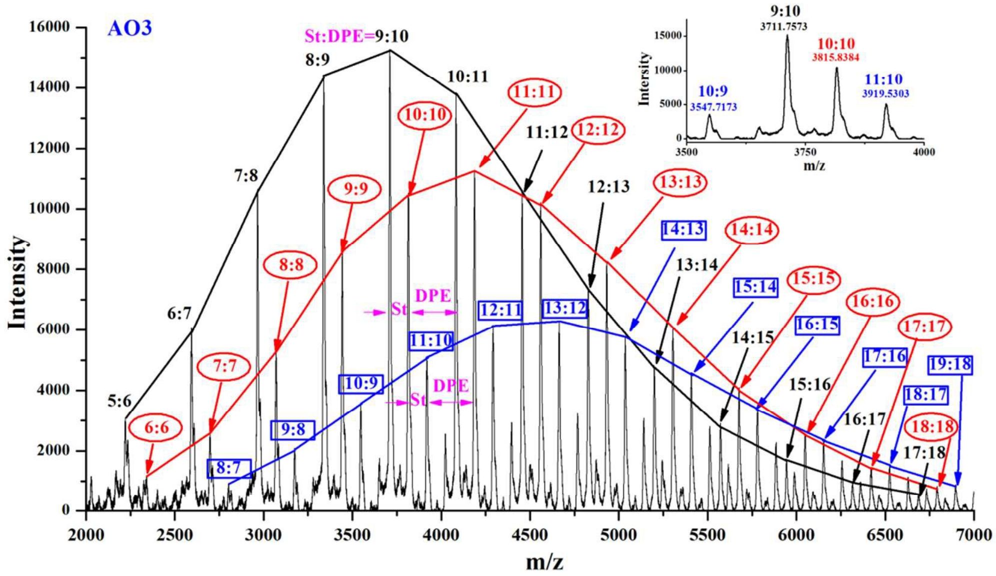


Fig. 13 MALDI-TOF mass spectrum for the copolymer of AO3.

of polymer chains some of which undoubtedly have an alternating sequence with peaks indicating a ratio of styrene:DPE repeat units of n-1:n, n:n and n:n-1. However, there are also significant peaks with comonomer ratios of n:n-2 and n:n-3 indicating a non-alternating comonomer sequence. The end effect cannot be ignored when the molecular weights are less than 5,000; the initiator (1,1-diphenylalkyllithiums) and end-capping agent in chain terminals are the corresponding DPE derivatives. Therefore, in theory, N_S/N_D should be less than 1.[15,45] Despite the trace amounts of styrene micro-blocks could not be eliminated completely, particularly when $r_S>1$ for DPE-D. Thus, copolymers of styrene and DPE-D with approximately alternating arrangements were synthesized. Good agreement was obtained between the MALDI-TOF MS and the statistical results.

The T_g of homopolymers of DPE-SiH/OMe and DPE-SiH/NMe$_2$ could also be calculated from Fox's equation (Equation 16 in Table 1S in ESI†).[38] The results are summarized and listed in Table 6. The theoretical values of average glass transition temperatures in the DPE-SiH/OMe homopolymer, $T_{g\text{-}O}^{th}$=192 °C and accordingly, $T_{g\text{-}N}^{th}$=229 °C calculated from these alternating copolymers using Equation 16; which correspond with the extrapolated values, $T_{g\text{-}O}^{ex}$=185 °C and $T_{g\text{-}N}^{ex}$=211 °C, calculated from Equations iii and iv. In contrast to the previous works,[38] the glass transition temperatures of the DPE-NMe$_2$ homopolymer, calculated from Equation 16, is T_g^{th}=217 °C, which means that the Si-H groups in DPE-SiH/NMe$_2$ could reduce chain motion and improve the copolymer's thermal stability despite its lower molecular weight.

The intermolecular alkaline functional groups, e.g., methoxy groups in DPE-SiH/OMe and dimethylamino groups in DPE-SiH/NMe$_2$, were also observed to be Lewis bases. However, they have only a slight effect on the copolymerization even though the molar feed ratios of $[M_D]_0/[I]$ are greater than 50 in AO3 and AN3. This conclusion corresponds well with the literature.[74]

In summary, the critical feed ratios for alternating copolymerization of styrene with DPE-SiH/OMe and styrene with DPE-SiH/NMe$_2$ were obtained by determining the reaction rate constants. Then, the corresponding approximately alternating copolymers that comply with the critical feed ratios were designed and synthesized. The precise alternating structures were characterized by ^{1}H-NMR, ^{13}C-NMR, and MALDI-TOF MS.

Conclusions

Two types of novel 1,1-diphenylethlene derivative monomers (DPE-SiH/OMe and DPE-SiH/NMe$_2$) containing asymmetric bi-functionalized groups were successful synthesized in this work. Subsequently, two types of copolymer, P(St-co-DPE-SiH/OMe) and P(St-co-DPE-SiH/NMe$_2$), were prepared via anionic polymerization. The in-chain functionalized polystyrenes with different amounts of functionalized DPE derivatives were obtained by varying the feed ratio. Each sample was characterized by SEC, and ^{1}H NMR. The average reactivity ratios, $r_{S\text{-}O}$=1.42 and $r_{S\text{-}N}$=1.79, were obtained and were similar to the results of the theoretical calculations using the Hammett equation. Furthermore, each sample was characterized by DSC, and the empirical relationships between the glass transition temperature of the copolymer (T_g) and the DPE derivative weight percent in the copolymer (DPE derivative wt%) were obtained. Furthermore, the extrapolated values of the glass transition temperatures for the homopolymers of the corresponding DPE derivatives, $T_{g\text{-}O}^{ex}$=180 °C and $T_{g\text{-}N}^{ex}$=211 °C, were obtained and are approximately equal to the theoretical value of $T_{g\text{-}O}^{th}$=192 °C and $T_{g\text{-}N}^{th}$=229 °C. Two types of reaction kinetics, the copolymerization of styrene and the corresponding DPE derivative at $[M_S]_0/[M_D]_0$=4, were investigated by time sampling, and the relevant kinetic curves were obtained. ^{1}H NMR, SEC and MALDI TOF MS were used to determine the statistical sequences of the corresponding copolymers, and average sequence diagrams of the chain propagations were obtained. To obtain the corresponding alternating copolymer, two types of theoretical critical molar feed ratios, $[M_S]_0^C/[M_O]_0^C$=0.74 and $[M_S]_0^C/[M_N]_0^C$=0.76, were obtained by studying the reaction kinetics. Consequently, approximately alternating copolymers of styrene and the corresponding DPE derivatives were obtained, and the monomer unit ratios (N_S/N_D) in the copolymers were 1.04 and 1.06, respectively. The partly alternating structures of the copolymers were proven using ^{1}H NMR, ^{13}C NMR and MALDI TOF MS.

A series of functionalized copolymers were prepared by LAP, and their backbones have functional groups that are introduced quantitatively and with position-control. Further work exploiting and applying these functionalized polymers is underway.

Acknowledgements

This work was financially supported by National Basic Research Program of China, Grant No. 2015CB654700 (2015CB654701) and National Natural Science Foundation of China (No.21304013 and No.21034001).

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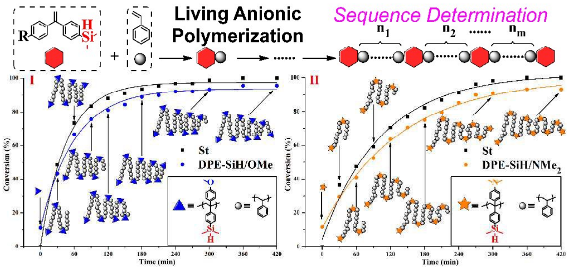
For graphical abstract use only

Title: Monomer Sequence Determination in the Living Anionic Copolymerization of Styrene and Asymmetric Bi-Functionalized 1,1-Diphenylethylene Derivatives

Authors: Wei Sang, Hongwei Ma, Qiuyun Wang, Xinyu Hao, Yubin Zheng, Yurong Wang, Yang Li*

Graphical Abstract:



Brief: In-chain functionalized polystyrenes with different sequential arrangements of functional groups are prepared via the living anionic copolymerization of styrene and asymmetric bi-functionalized DPE derivatives. The sequence structures are determined by time sampling to establish the sequence-determination method.