

# Regio-Specific Polyacetylenes Synthesized from Anionic Polymerizations of Template Monomers

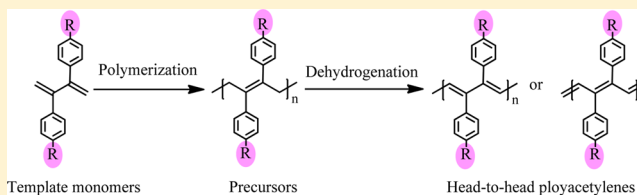
Yang Zhang,<sup>†</sup> Jia Li,<sup>†</sup> Xiaohong Li,<sup>‡</sup> and Junpo He<sup>\*,†</sup>

<sup>†</sup>The State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

<sup>‡</sup>College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China

## S Supporting Information

**ABSTRACT:** Substituted polyacetylenes with alkylphenyl side groups and head-to-head regioregularity were prepared through anionic living polymerization of template monomers and subsequent dehydrogenation process. The template monomers have the structure of 2,3-disubstituted-1,3-butadienes prepared by palladium-catalyzed Kumada coupling of the corresponding vinyl bromides. Anionic polymerizations of the template monomers produced narrow disperse substituted polybutadiene precursors with exclusive 1,4-enchainment. The precursors were converted into soluble polyacetylene derivatives via two methods, e.g., bromination followed by elimination of HBr, and direct dehydrogenation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), both resulting in dark colored products with significant red shift in UV spectra. The obtained head-to-head polyacetylene derivatives exhibited highly thermal stability, possibly due to *trans*-rich and/or head-to-head chain configurations. The microstructures of the poly(2,3-dialkylphenyl butadiene) precursors were analyzed in detail using NMR spectroscopy with regard to the solvent effect during polymerization. Block copolymers containing substituted polyacetylene segments were prepared through sequential anionic polymerization of different monomers, followed by dehydrogenation transformation. The present synthesis may serve as a new strategy for tailoring molecular structures of polyacetylene-based polymers by virtue of anionic living polymerization techniques.



## INTRODUCTION

Polymers are characterized by a number of molecular parameters such as chemical composition, microstructure, topological structure, molecular weight and polydispersity, and electronic structure as well as molecular conformation.<sup>1</sup> These factors work on different levels concurrently, rendering polymer materials a great diversity of properties. It has been a long-standing goal to control molecular structural parameters as many as possible in a single polymerization system. Nevertheless, the conventional polymerization techniques usually show limited ability of controlling various chain structures simultaneously. For instance, Ziegler–Natta catalyst is able to control the stereoregularity but not molecular weight, whereas anionic polymerization yields block copolymers with precise molecular weights but not specificity in chain microstructure.

Polymer chain microstructure usually concerns three types of isomerism, e.g. positional, stereo, and geometrical isomerism.<sup>1</sup> Positional isomerism describes the connection of the repeating units in a polymer chain of vinyl monomer, i.e., head-to-tail or head-to-head enchainment. Conventional addition polymerizations yield predominantly head-to-tail products due to resonance stabilization and steric effects in the propagation steps. Regio-specific head-to-head polymers can only be synthesized through monomer design or postmodification of 1,4-polydienes or alternating copolymers.<sup>2</sup> The former strategy employs a template monomer, such as 2,3-disubstituted-1,4-

butadiene, as a precursor for the head-to-head dimeric units after hydrogenation.<sup>3</sup> In the postmodification approach, for example, chlorination or bromination of 1,4-polydienes results in the formation of head-to-head polyvinyl chloride (PVC) or polyvinyl bromide (PVB), respectively.<sup>4</sup> On the other hand, stereo isomerism describes the stereo regularity of polymers containing chiral center on the main chain, such as polypropylene prepared by Ziegler–Natta or metallocene catalysts;<sup>5</sup> Geometrical isomerism refers to the *cis* and *trans* configurations of polydienes which can be controlled by transition metal catalysts.<sup>6</sup>

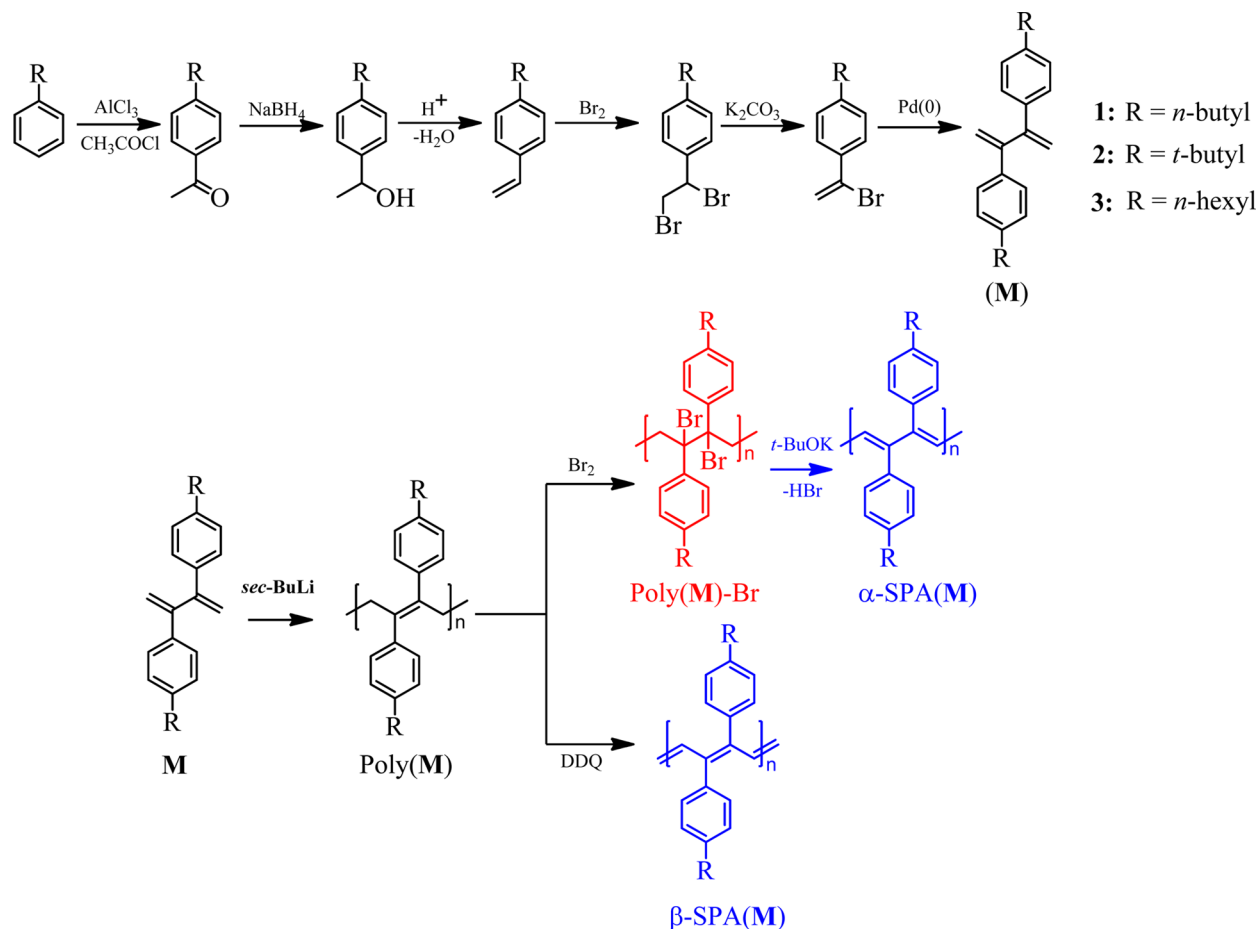
In the present work, we focus on the synthesis of regio-specific monosubstituted polyacetylenes through anionic polymerization of 2,3-disubstituted-1,3-butadiene as a template monomer followed by dehydrogenation. Previously, substituted polyacetylenes (SPA) with various side groups were prepared through polymerizations of substituted acetylenes using transition metal (Mo, W, and Rh, etc.) catalysts, rendering the products improved solubility, processability as well as functional properties.<sup>7</sup> Ring-opening metathesis polymerization of monosubstituted cyclooctatetraenes also led to the formation of partially substituted polyacetylenes.<sup>8</sup> The unique feature of

Received: June 22, 2014

Revised: August 18, 2014

Published: September 14, 2014

Scheme 1. Synthesis of Substituted Polyacetylenes from Anionic Polymerization of Template Monomers



the products in the present work is their head-to-head regiospecificity, which may influence chain conformation and electron conjugation property.

Both radical and anionic polymerizations of 2,3-diphenyl-1,3-butadiene were reported previously, and the products were hydrogenated to make head-to-head polystyrenes by Vogl et al.<sup>9</sup> and Hirao et al.<sup>10</sup> The radical polymerization products were readily soluble in organic solvents, whereas the products of anionic polymerization showed a tendency of precipitation from most organic solvents on standing, except hot *o*-dichlorobenzene or toluene, possibly due to crystallization of the products.

Anionic polymerization is a traditional living polymerization technique for precisely controlling the chain length, composition and architecture of polymers. It has been employed to prepare poly(vinyl sulfoxides), a precursor polymer for polyacetylene after side group elimination.<sup>11</sup> On the other hand, butadiene derivatives are readily polymerized by anionic polymerization. Bromination of the residual double bond and subsequent dehydrobromination can produce polyacetylene derivatives.<sup>12</sup> Thus, substituted 1,3-butadienes can serve as template monomers in the preparation of substituted polyacetylenes. Design of substituents in monomers will provide many possibilities for molecular design of substituted polyacetylene, in addition to the precise control on molecular weight, molecular weight distribution, and block copolymerization facilitated by anionic polymerization.

## RESULTS AND DISCUSSION

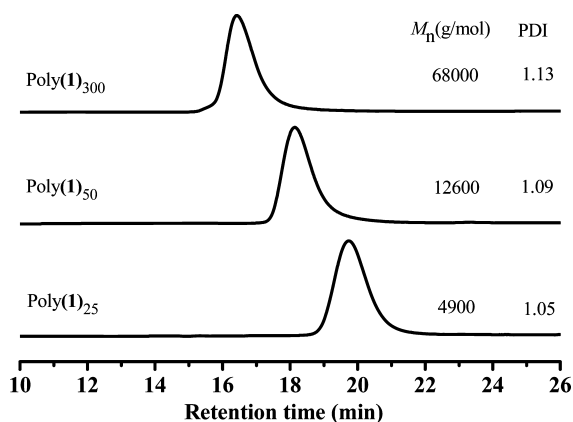
The synthetic route of head-to-head polyacetylenes is based on anionic polymerizations of 2,3-disubstituted-1,3-butadienes followed by dehydrogenation. In order to increase the solubility of the polymerization products, we used alkylphenyls as the substituents in which the alkyl groups are *n*-butyl, *tert*-butyl and *n*-hexyl, respectively. The dehydrogenation is accomplished either by a two-step process of bromination and dehydrobromination or by direct treatment of the polymerization product with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). The resulting substituted polyacetylenes of the two-step processes and the direct method are designated as  $\alpha$ - and  $\beta$ -SPA, respectively. The overall synthetic processes, including monomer synthesis, are shown in Scheme 1.

**Monomer Synthesis, Polymerizations, and Transformation Reactions.** *Monomer Synthesis.* The butadiene monomers with 2,3-dialkylphenyl substituents were synthesized through Kumada coupling of  $\alpha$ -bromo(4-alkyl)styrene using palladium catalyst,<sup>13</sup> with the overall yields usually in the range of 10–15%. Three monomers with side groups of *n*-butylphenyl (**1**), *tert*-butylphenyl (**2**), and *n*-hexylphenyl (**3**) were obtained as colorless liquids (**1** and **3**) or crystal (**2**), and characterized by FT-IR, <sup>1</sup>H NMR, and mass spectroscopies. The synthetic results of  $\alpha$ -bromo(4-alkyl)styrene and the butadiene monomers **1**, **2** and **3** are listed in Experimental Section and Supporting Information.

*Homopolymerizations.* Anionic polymerizations of monomers were carried out using *s*-BuLi as the initiator in different

solvents, e.g., cyclohexane, THF, or their mixture. In cyclohexane, the reaction mixture displayed a red color throughout the polymerization process. However, the polymerization rate was slow. A conversion of 55% was measured after the polymerization stood for 8 h. In THF, the solution became dark-red in color upon addition of the initiator, and the polymerization was complete after 2 h. Nonetheless, the reaction temperature had to be kept at  $\sim -80\text{ }^{\circ}\text{C}$  in this system. A better choice was to perform the reaction in cyclohexane with trace amount of THF at  $40\text{ }^{\circ}\text{C}$  (THF/Li = 10/1 molar ratio). A complete conversion of monomer was fulfilled within 2 h. The polymerization was quenched by deaerated methanol. All of the products from various reaction solutions were readily soluble in most organic solvents such as cyclohexane, THF, dichloromethane and chloroform, in contrast to the system without alkyl groups in the literature.<sup>9,10</sup> Vogl obtained insoluble product from the polymerization of 2,3-diphenyl-1,3-butadiene initiated by sodium naphthalene in THF.<sup>9</sup> Hirao et al. observed that the product from the same monomer precipitated completely from the reaction solution (THF) upon standing for a few hours.<sup>10</sup>

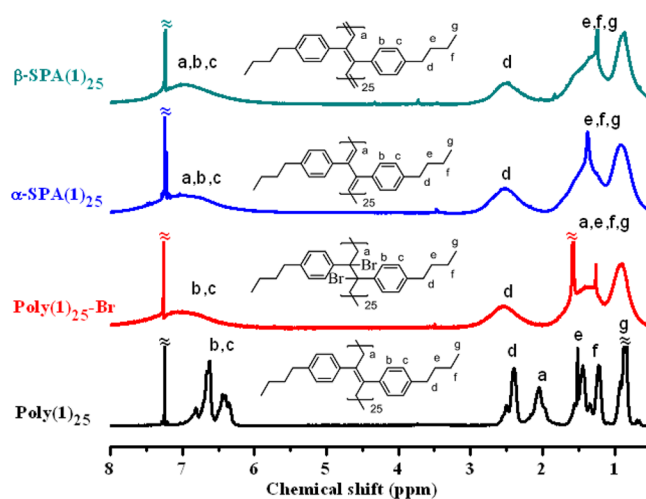
In the following, we will focus on the results of polymerization of **1** in mixed solvents cyclohexane/THF, except otherwise stated. Figure 1 shows GPC curves of poly(**1**)



**Figure 1.** GPC curves of poly(**1**) prepared from anionic polymerizations at different ratios of monomer/initiator (as shown in Table 1).

from anionic polymerizations with varying ratio of **1**/*s*-BuLi. The peak shifts to larger molecular weight with increasing ratio of monomer to initiator, while the polydispersity index remains low. The  $M_w$  values measured by multiangle laser light scattering detector are close to the theoretical ones, as shown in Table 1. Living anionic polymerizations of monomer **2** and **3** also worked well under similar conditions.

**Bromination of the Backbone and Subsequent Elimination of HBr.** Bromination of the backbone unsaturations in precursor polymers was carried out in dichloromethane according to literature method.<sup>4</sup> Excessive bromine was used and the reaction proceeded at  $0\text{ }^{\circ}\text{C}$  for 4 h. After the reaction, the products were precipitated in methanol and greenish brown colored powders were obtained. Elementary analysis showed Br content of 32.76%, indicating a conversion of 98% in correlation with the theoretical value 33.41%.  $^1\text{H}$  NMR spectra of the polymer before and after bromination (Figure 2) also



**Figure 2.**  $^1\text{H}$  NMR spectra of precursor polymer, poly(**1**)<sub>25</sub>, brominated product, poly(**1**)<sub>25</sub>-Br, and  $\alpha$ - and  $\beta$ -type polyacetylenes (in  $\text{CDCl}_3$ ).

showed the disappearance of the main chain allylic protons at 1.7–2.2 ppm. However, the signals after bromination became broad, possibly due to the steric hindrance caused by Br atom impeding free rotation of the C–C single bond. In addition, the GPC peaks of the brominated products shifted to lower

**Table 1.** Characterization Results of the Precursor Polymers, the Bromination Products, and the Corresponding Substituted Polyacetylenes

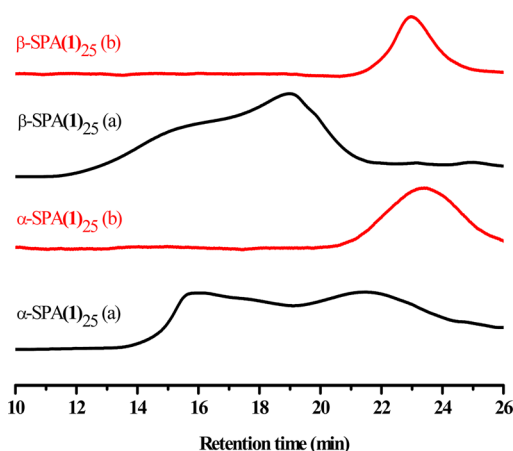
samples	s-BuLi (mmol)	monomer (mmol)	$M_{n,\text{calcd}}$ ( $\times 10^3$ g/mol)	$M_{n,\text{GPC}}$ ( $\times 10^3$ g/mol)	$M_{w,\text{MALLS}}$ ( $\times 10^3$ g/mol)	PDI <sub>GPC</sub>
poly( <b>1</b> ) <sub>25</sub>	0.13	3.20	8.0	4.9 <sup>a</sup>	7.9	1.05 <sup>a</sup>
poly( <b>1</b> ) <sub>25</sub> -Br			12.0	5.9 <sup>a</sup>		1.14 <sup>a</sup>
$\alpha$ -SPA( <b>1</b> ) <sub>25</sub>			8.0	2.4 <sup>b</sup>		2.26 <sup>b</sup>
$\beta$ -SPA( <b>1</b> ) <sub>25</sub>			8.0	3.2 <sup>b</sup>		1.65 <sup>b</sup>
poly( <b>1</b> ) <sub>50</sub>	0.13	6.50	16.0	12.6 <sup>a</sup>	18.1	1.09 <sup>a</sup>
poly( <b>1</b> ) <sub>50</sub> -Br			23.9	11.5 <sup>a</sup>		1.37 <sup>a</sup>
$\alpha$ -SPA( <b>1</b> ) <sub>50</sub>			16.0	2.2 <sup>b</sup>		2.56 <sup>b</sup>
$\beta$ -SPA( <b>1</b> ) <sub>50</sub>			16.0	5.5 <sup>b</sup>		1.77 <sup>b</sup>
poly( <b>1</b> ) <sub>300</sub>	0.13	40.00	95.5	68.0 <sup>a</sup>	91.0	1.13 <sup>a</sup>
poly( <b>1</b> ) <sub>300</sub> -Br			143.3	18.6 <sup>a</sup>		1.66 <sup>a</sup>
$\alpha$ -SPA( <b>1</b> ) <sub>300</sub>			95.5	1.8 <sup>b</sup>		3.17 <sup>b</sup>
$\beta$ -SPA( <b>1</b> ) <sub>300</sub>			95.5	7.0 <sup>b</sup>		1.94 <sup>b</sup>

<sup>a</sup>Results of conventional GPC. <sup>b</sup>Results of high temperature GPC.

molecular weight value and became broad, as shown in Supporting Information (Figure S1). Thus, the GPC measured molecular weight after bromination was much lower than the theoretical value (Table 1). Light scattering technique gives real molecular weight of polymers. Unfortunately, the measurement of light scattering failed due to light absorption of the present samples.

Elimination of HBr was performed in THF solution at room temperature in the presence of *t*-BuOK. The reaction mixture turned into dark brown in color immediately upon addition of the base. After the reaction, the product was collected through dialysis in water. The resulting substituted polyacetylene with *n*-butyl side chain,  $\alpha$ -SPA(1), formed dark brown colored stable solutions or dispersions in common solvents such as THF, toluene, dichloromethane, cyclohexane, and chloroform. Elemental analysis using XPS technique gave a residual Br of 0.72% in  $\alpha$ -SPA(1)<sub>25</sub>, indicating 2% of unconverted repeating units (Supporting Information Table S2). <sup>1</sup>H NMR in Figure 2 shows that, after elimination, the signal of main chain ethylene at 1.6 ppm disappeared, whereas the signal of the resulting olefinic protons (expected  $\delta$  = 5.82 ppm for *cis*-transoidal and 6.85 ppm for *trans*-cisoidal) overlapped with those of aromatic protons in the range of chemical shift 5.6–8.0 ppm.<sup>14</sup> The small intensity of the peak at  $\delta$  = 5.82 ppm is negligible, therefore *trans* structure is the dominant configuration in the product.

The GPC results of the elimination reaction products are shown in Figure 3. All of GPC curves display extremely broad



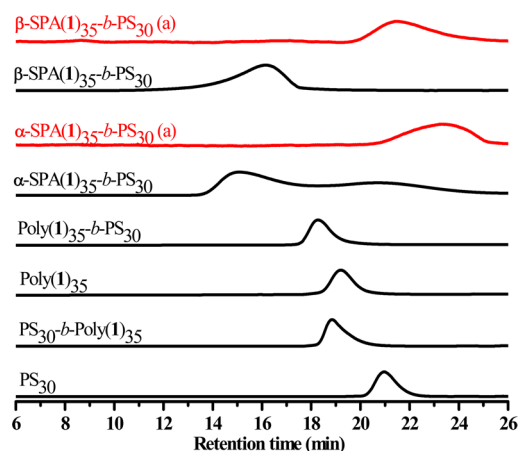
**Figure 3.** Conventional (a) and high-temperature (b) GPC curves of  $\alpha$ -SPA(1)<sub>25</sub> and  $\beta$ -SPA(1)<sub>25</sub>.

multimodal distribution, with the highest molecular weight tail far exceeding the upper limit of the column resolution. These observations may indicate aggregation of  $\alpha$ -SPA(1) in THF solution due to  $\pi$ – $\pi$  interaction despite of the presence of the side chains. It was reported that high temperature can help to dissolve  $\pi$ -conjugated polymers and thus obtaining monomodal GPC profiles.<sup>12,13</sup> Thus, we carried out high temperature GPC using 1,2,4-trichlorobenzene as the eluent at 150 °C. Indeed, unimodal peaks were observed for all of the products in spite of relative broad distribution. The characterization data in Table 1 shows that the molecular weights ( $M_{n,GPC}$ ) determined by high-temperature GPC (in relative to polystyrene standard) are remarkably lower than the calculated ( $M_{n,calc}$ ). We are not sure about whether there is chain linking and/or cleavage during the bromination/dehydrobromination process. This concern arises from the above-mentioned uncertainty in molecular weight

measurement. Hydrogenation of the precursor and SPA into saturated polymer species may serve as a potential method for molecular weight determination.<sup>15</sup> This need, however, a systematic study to find suitable selective hydrogenation reactions in the future.

**Direct Dehydrogenation by DDQ.** Although it seems that the two step process worked well, there was still less than 2% (weight percent) bromine residue as indicated by elementary analysis for the product after HBr elimination (Supporting Information, Table S2). Thus, direct dehydrogenation of the precursors was also performed using DDQ as the dehydrogenation agent at 90 °C in toluene, resulting in  $\beta$ -type conjugated structure ( $\beta$ -SPA). In general, the characterization results of  $\beta$ -SPA are very similar to those of  $\alpha$ -SPA, indicating high similarity in the molecular structure. As shown in Figure 3, the normal GPC profile is also very broad but the peaks shifts to larger molecular weight region in relative to that of  $\alpha$ -SPA. High temperature GPC shows a narrower, lower molecular weight peak at a close elution time as that of  $\alpha$ -SPA.

**Block Copolymerization.** The present anionic strategy of making substituted polyacetylenes can be easily applied for the synthesis of block copolymers containing SPA segments. Therefore, styrene was used as comonomer to block copolymerize with 2,3-disubstituted butadienes. The cross initiation of styrene by the anion of poly(1), or *vice versa*, went smoothly, resulting in further chain growth with monomer conversion (Figure 4). The products were obtained



**Figure 4.** GPC curves of the first block, the block copolymers of styrene and monomer 1 with different block sequence, and block copolymers after dehydrogenation containing  $\alpha$ - and  $\beta$ -SPA(1) segments (all black lines). The red lines (a) are results of high-temperature GPC of the corresponding block copolymers containing SPA segments.

quantitatively in both systems. The molecular weights measured by GPC were summarized in Table 2. Hirao et al. observed block sequence selectivity in the copolymerization in pure THF, e.g., polystyrenyl anion was able to initiate the polymerization of 2,3-diphenyl-1,3-butadiene, but not the reverse.<sup>10</sup> The difference between the present results with that in literature may arise from the polarity of the solvent. The mixed solvent used in this work has a medium polarity and thus allows an appropriate initiation rate in relative to that of the propagation.

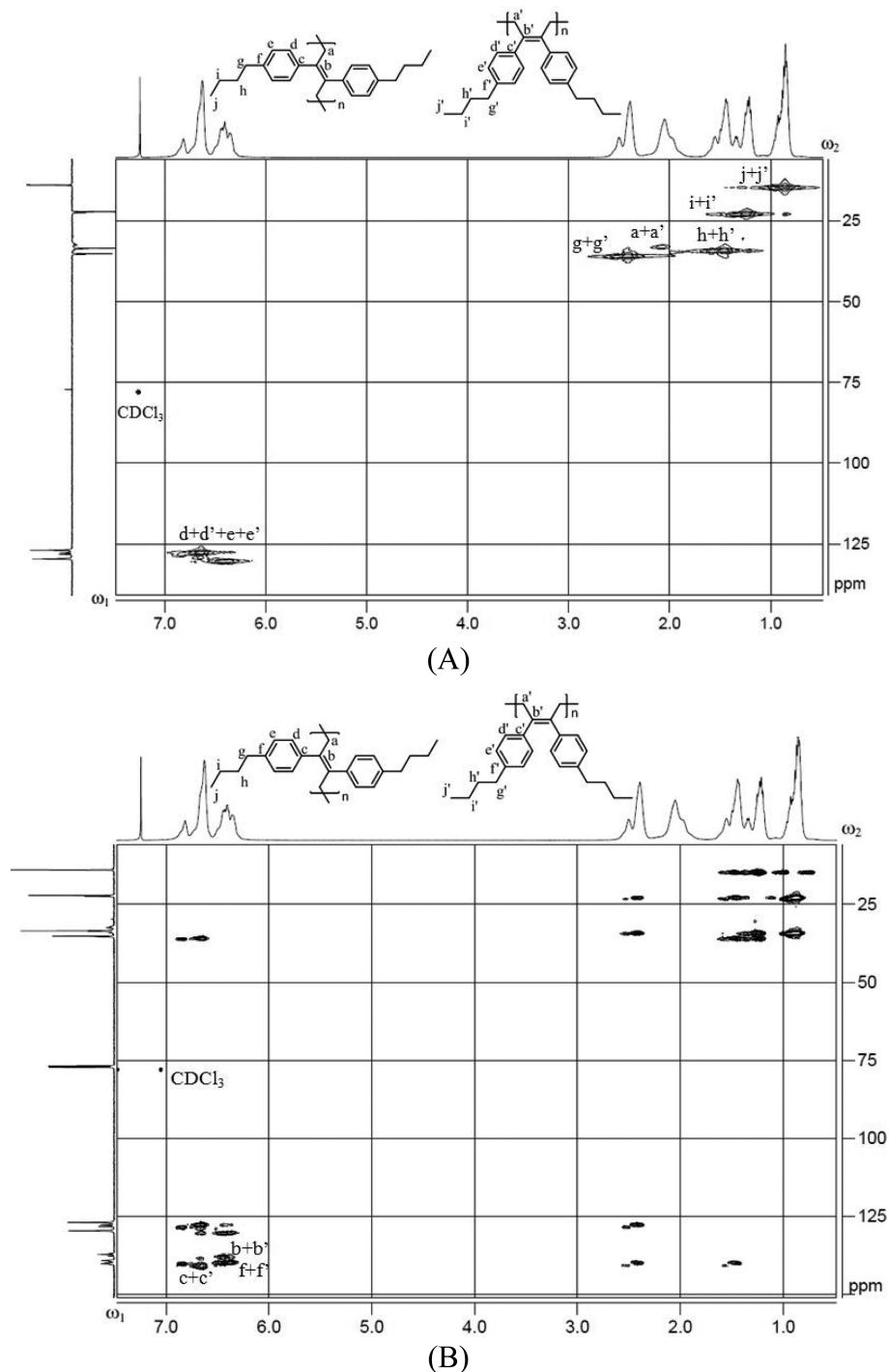
The poly(1) segment of the block copolymer can also be converted into SPA(1) block through either bromination/

**Table 2.** Characterization of Block Copolymers and the Precursors

sample	$M_{\text{calc}}$ ( $10^3$ g/mol)	$M_n$ ( $10^3$ g/mol)	PDI
PS <sub>30</sub>	3.1	3.3 <sup>a</sup>	1.05
PS <sub>30</sub> - <i>b</i> -poly(1) <sub>35</sub>	14.3	12.5 <sup>a</sup>	1.15
poly(1) <sub>35</sub>	11.1	8.8 <sup>a</sup>	1.09
poly(1) <sub>35</sub> - <i>b</i> -PS <sub>30</sub>	14.3	13.8 <sup>a</sup>	1.14
$\alpha$ -SPA(1) <sub>35</sub> - <i>b</i> -PS <sub>30</sub>	14.3	2.3 <sup>b</sup>	2.95
$\beta$ -SPA(1) <sub>35</sub> - <i>b</i> -PS <sub>30</sub>	14.3	3.4 <sup>b</sup>	3.21

<sup>a</sup>Results of conventional GPC. <sup>b</sup>Results of high temperature GPC.

dehydrobromination or direct dehydrogenation process. After the two step reactions, the white powder of the block copolymer precursor became dark brown in color after precipitation from methanol. Figure 4 also shows the conventional (a) and high-temperature (b) GPC curves of  $\alpha$ - and  $\beta$ -SPA(1)<sub>35</sub>-*b*-PS<sub>30</sub>. The conventional GPC curves are broad distribution that may arise from the aggregates despite the presence of soluble PS blocks. Again, high temperature GPC shows monomodal distribution (the red lines), but the polydispersity index is remarkably larger than 1.5.

**Figure 5.** HSQC (A) and HMBC (B) spectra of poly(1)<sub>25</sub>.



**Structural Analysis of the Polymeric Products.** Chain microstructures of the precursor, the brominated intermediates, and the two types of the resulting SPAs ( $\alpha$ - and  $\beta$ -), were investigated using  $^1\text{H}$  NMR. The results in Figure 2 show completely no signal in the range of  $\delta = 4.5$ – $5.5$  ppm (for pendent vinylic protons), indicating that the microstructure contains nearly 100% 1,4-enchainment. Polymerizations of different monomers gave similar results which were independent of solvents, e.g., cyclohexane or THF (Supporting Information Figure S2). This agrees with previous report on anionic polymerization of 2,3-diphenyl-1,3-butadiene.<sup>10</sup> The high selective enchainment is a consequence of steric hindrance at 2- and 3-position of the monomers.

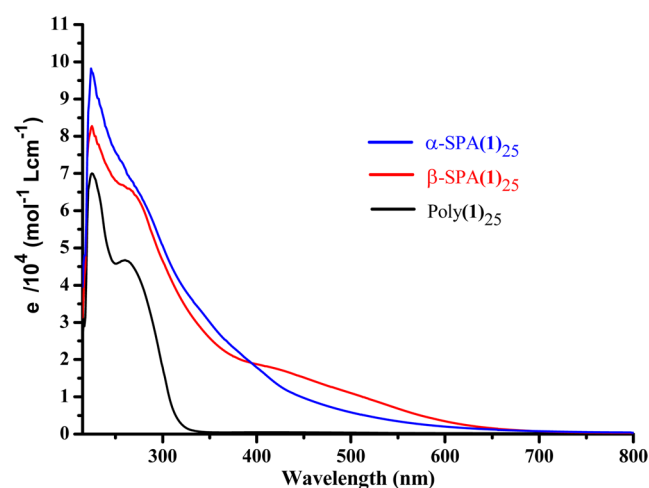
Detailed assignments of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of poly(1)<sub>25</sub> were performed using two-dimensional NMR, heteronuclear singular quantum correlation (HSQC) and the heteronuclear multiple bond correlation (HMBC). As shown in Figure 5, the  $^1\text{H}$  signals between  $\delta = 0.75$ – $1.65$  and  $2.30$ – $2.65$  ppm and the  $^{13}\text{C}$  signals between  $\delta = 14.0$ – $36.0$  ppm are easily assigned to butyl side group. Allylic carbon on the main chain ( $-\text{CH}_2-\text{CH}_2-$ ) shows broad proton signals at around 2.1 ppm in correlation with a very weak  $^{13}\text{C}$  signal at 34.2 ppm. By comparing the spectra of HSQC and HMBC, it is clear that the aromatic protons and carbons at the positions of d, d', e, and e' show signals at  $\omega_1 = 6.2$ – $7.0$  ppm and  $\omega_2 = 126.9$ – $129.7$  ppm, respectively, whereas the tertiary aromatic carbons f, f', c, and c' give signals at  $\omega_2 = 139.2$  and  $\omega_2 = 140.2$  ppm, respectively. In addition, the vinylic carbon of the main chain (b + b') appears at  $\omega_2 = 137.2$  ppm. Surprisingly, no crosspeak was observed for the main chain methylene groups ( $\omega_1 = 2.1$  ppm) with any carbon atoms in the HMBC spectra. The reason is not clear from the current results.

On the basis of structural analysis, we are able to estimate the configuration of the precursor main chain using  $^{13}\text{C}$  NMR shown in Figure 6. Close inspect of the spectra indicates that all the butyl-phenyl, main chain methylene and olefinic signals appear to be doublet due to geometric isomers in the main chain. According to Vogl's analysis for poly(2,3-diphenylbutadiene), main chain methylene carbon showed a doublet at 32.2

and 30.6 ppm for *trans* and *cis* configurations, respectively, whereas phenyl C<sub>1</sub> showed a doublet at 140.0 (*trans*) and 140.5 (*cis*) ppm, respectively.<sup>9</sup> On this basis, we assign peaks at 34.3 and 32.5 ppm for main chain methylene carbon in *trans* and *cis* isomers, while peaks at 140.1 and 139.9 ppm for phenyl C<sub>1</sub> in *cis* and *trans* isomers, respectively. Actually, all these doublets show similar trends in the dependence of *cis/trans* ratio on the polymerization solvents, although some of them are partially overlapped.

We choose signal of carbon i+i' (in Figure 6) for calculation of *cis/trans* ratio because the doublet are well separated. The peaks at 22.5 and 22.1 ppm are attributed to butyl groups of *trans* and *cis* isomers. Their relative intensity depends on polymerization solvents, the *cis/trans* ratio being 20/80, 45/55 and 75/25 for the products from cyclohexane, cyclohexane/THF and pure THF, respectively. The dissolving behavior of these products in THF is different, e.g., product with highest *trans* content dissolves slowly while product with medium or low *trans* content dissolves immediately in THF. This may indicate that poly(1) chain tends to aggregate through  $\pi$ - $\pi$  interaction in *trans* configuration.

Figure 7 shows the UV spectra of the precursor and the corresponding substituted polyacetylenes (both  $\alpha$ - and  $\beta$ -types).



**Figure 7.** UV spectra of THF solutions of Poly(1)<sub>25</sub>,  $\alpha$ -SPA(1)<sub>25</sub>, and  $\beta$ -SPA(1)<sub>25</sub>.

Strong absorptions above 350 nm were observed for the product after dehydrogenation due to the  $\pi$ - $\pi^*$  electronic transition of the main chains.<sup>16</sup> The two type of SPAs showed similar spectral patterns despite of slight difference in the range of 400–650 nm.

**Thermal stability.** One of the most important issues for substituted polyacetylenes is their thermal stability. The *cis-transoidal* isomeric structure of substituted polyacetylenes undergoes thermal decomposition through an electrocyclization mechanism (eq 1), resulting in chain scission and releasing trisubstituted benzene as a byproduct.<sup>17</sup>

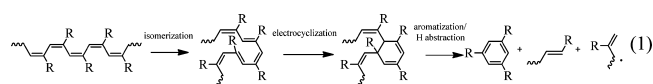
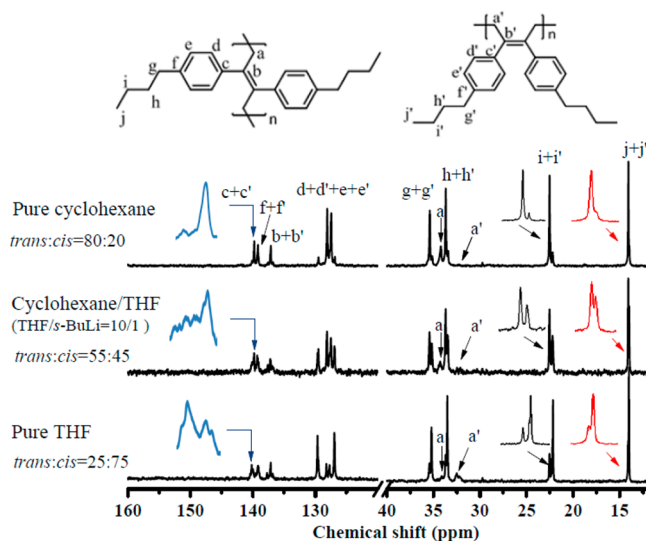
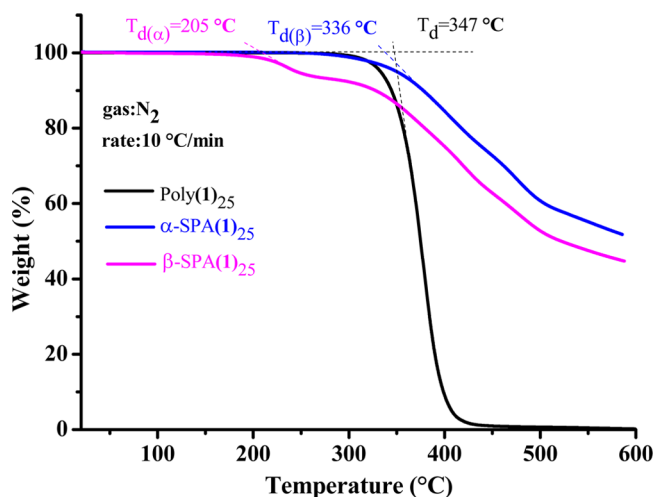


Figure 8 shows the TGA curves of  $\alpha$ - and  $\beta$ -SPA(1)<sub>25</sub> as well as that of the precursor measured under nitrogen atmosphere. While the precursor decomposed completely at 450 °C, the



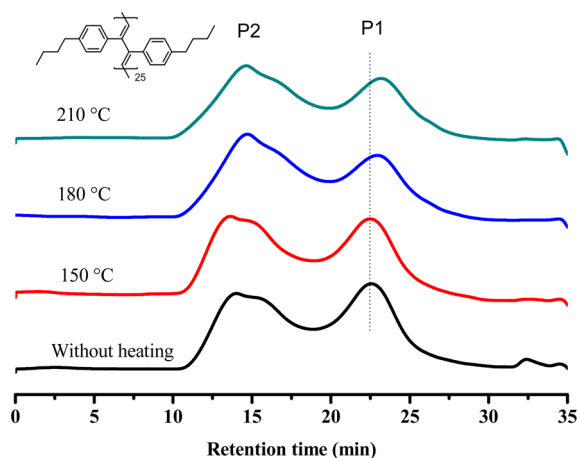
**Figure 6.**  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$ ) of poly(1) prepared in various polymerization media. The insets are partial enlargement of concerned doublets resulted from different configurations.



**Figure 8.** TGA thermograms of poly(1)<sub>25</sub>, α-SPA(1)<sub>25</sub>, and β-SPA(1)<sub>25</sub>.

substituted polyacetylenes leave ca. 44–52% residue at a temperature up to 600 °C. It is noticed that α-type product is more stable than β-type, with 130 °C higher setup temperature and 8% larger weight retention.

Thermal stability of the resulting polyacetylenes was also investigated by heating a black powder of α-SPA(1)<sub>25</sub> in a flask under nitrogen atmosphere. After heating at 150 °C for 2 h, the black powder was cooled to room temperature, dissolved in THF and subjected to GPC analysis. As shown in Figure 9, no



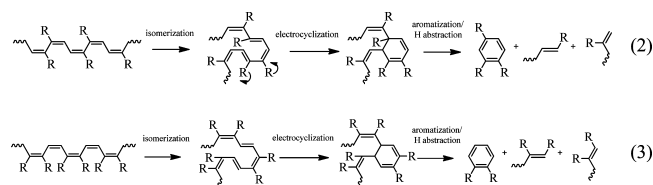
**Figure 9.** GPC curves of α-SPA(1)<sub>25</sub> after heat treatment for 2 h.

notable change in the multimodal GPC curves is observed. When the heating temperature being raised to 180 and 210 °C, the peaks shift slightly to low molecular weight region, possibly associated with the chain scission reaction. In contrast, heating β-SPA(1)<sub>25</sub> at 150 °C or higher temperature resulted in a product which was insoluble in THF.

Online NMR was also performed to trace a system of heating α-SPA(1)<sub>25</sub> in deuterated tetrachloroethane. Figure 10 shows the spectra obtained in the temperature range from 25 to 130 °C. Along with the temperature increase, the signal at 1.8 ppm becomes narrower and shifts to lower field. Nevertheless, there is no sharp signal appearing in the aromatic region, in spite of small peaks within  $\delta = 3.5\text{--}3.8$  ppm. This indicates that the decomposition is not remarkable and, if any, is not through

reaction 1. In general, the product in the present work shows high thermal stability.

We address the high thermal stability of the SPAs in the present work for two reasons. The first is that the products show *trans*-rich configuration, as indicated by NMR results, which is much more stable than *cis* isomer.<sup>18</sup> Second, the steric hindrance of head-to-head connectivity may inhibit the electrocyclization reaction in α-SPA(1)<sub>25</sub>. As shown in eq 2,



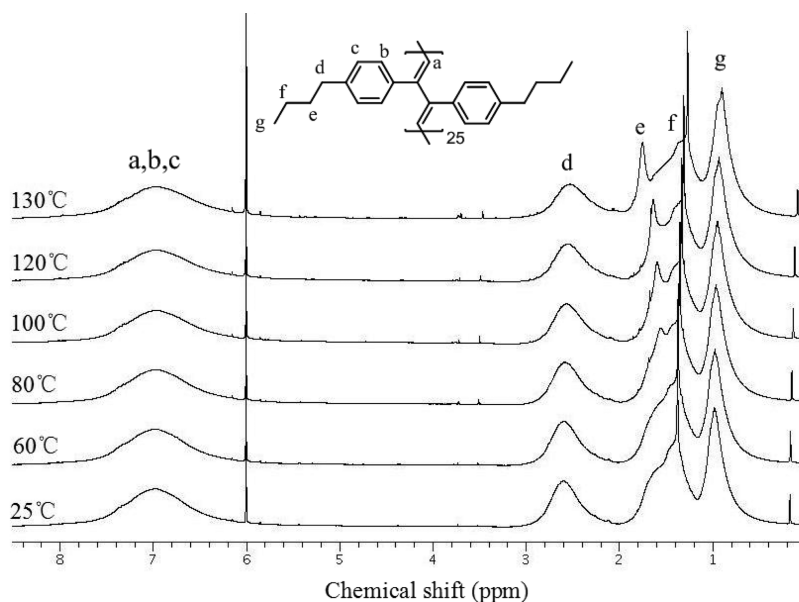
the bulkiness of the substituents prevent the coplanarity of the folded conformation, therefore preventing the formation of the cyclic intermediate. For β-SPA(1)<sub>25</sub>, however, the substituents are attached to the 1,2-position of the same double bond, forming a stilbene structure, which has smaller effect on the conformation (eq 3). Thus, α-SPA(1) is more stable than β-analogue as observed in TGA thermograms (Figure 8).

## CONCLUSION

The anionic polymerization of 2,3-disubstituted-1,3-butadienes is highly selective in cyclohexane, THF and their mixture, producing polymers with 1,4-connectivity. The ratio of *trans/cis* configuration of the resulting polymers depends on the polymerization media. These polymer precursors can be easily converted into substituted polyacetylenes with head-to-head regio structure through dehydrogenation. Two types of substituted polyacetylenes were prepared via either a two step process, bromination and dehydrobromination (resulting in α-SPA), or direct dehydrogenation in the presence of DDQ (resulting in β-SPA). While the precursors are narrow disperse, the corresponding substituted polyacetylenes exhibit very broad multimodal GPC profiles which extend to extremely large molecular weight region. This could be a consequence of polyacetylene chain aggregation. High temperature GPC can alleviate this tendency, giving monomodal GPC profiles with lower molecular weights. The thermal stability of the substituted polyacetylenes prepared in this work was high, possibly due to head-to-head regio-specificity and/or high content of *trans* configuration. Block copolymerizations of the template monomer and a traditional monomer, styrene, were achieved, and the products were convertible into block copolymers containing substituted polyacetylene segment. The cross initiation of both block sequence occurred smoothly. Preparation of polyacetylenes with other side groups, such as thienyl and pyrenyl, etc., are currently under investigation in our laboratory.

## EXPERIMENTAL SECTION

**Materials.** Tetrakis(triphenylphosphine) palladium ( $\geq 99\%$ ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ,  $\geq 98\%$ ) were purchased from Aldrich and used as received. *n*-Butylbenzene ( $\geq 99\%$ ), *n*-hexylbenzene ( $\geq 98\%$ ), *tert*-butylbenzene ( $\geq 99\%$ ), acetyl chloride ( $\geq 99\%$ ), sodium borohydride ( $\geq 99\%$ ), *p*-toluenesulfonic acid ( $\geq 99\%$ ), and aluminum chloride ( $\geq 99\%$ ) were purchased from National Pharmaceutical Co. and used as received. Potassium *tert*-butoxide ( $\geq 99\%$ ) was purchased from TCI and used as received. *sec*-Butyllithium (*s*-BuLi) (Aldrich, 1.0 M solution in cyclohexane/hexane) was titrated before use. Tetrahydrofuran (THF) were refluxed over



**Figure 10.** Online NMR spectra monitoring processes of heating  $\alpha$ -SPA(1)<sub>25</sub> up to 130 °C in deuterated tetrachloroethane.

sodium with benzophenone as indicator, and distilled from 1, 1-diphenylhexyllithium (DPELi, adduct of *s*-BuLi with 1,1-diphenylethylene) on the vacuum line before use. Styrene was distilled over di-*n*-butylmagnesium (MgBu<sub>2</sub>) (Aldrich, 1.0 M in hexane) on the vacuum line before use.

**Monomer Synthesis. Preparation of 4-*n*-Butylacetophenone.** The synthesis was performed according to the literature<sup>19</sup> in a 500 mL 3-neck flask fitted with a dropping funnel and a nitrogen inlet. Dry dichloromethane (100 mL) and *n*-butylbenzene (13.4 g, 100.0 mmol) were mixed in the flask and cooled to 0 °C in an ice/water bath. Aluminum trichloride (16.0 g, 120.0 mmol) was added, followed by dropping acetyl chloride (8.6 g, 110.0 mmol) over 15 min. The reaction mixture was stirred for 2 h, then poured into 1 L ice/water. The aqueous layer was extracted three times using dichloromethane (3 × 50 mL). The collected organic layer was washed with 200 mL saturated sodium chloride until the solution is neutral. The solution was dried with anhydrous sodium sulfate. After being concentrated, a colorless liquid was obtained. Yield: 17.0 g (97.0%). The product was used directly in the next step reaction.

**Preparation of 1-(*n*-Butylphenyl)ethyl Alcohol.** The synthesis was performed according to literature<sup>19</sup> in a 250 mL 3-neck flask fitted with a reflux condenser and a nitrogen inlet. The product in the last step, 4-*n*-butylacetophenone (17.0 g, 96.6 mmol), and NaBH<sub>4</sub> (7.6 g, 200.0 mmol), CH<sub>3</sub>OH (15 mL) were dissolved in THF (100 mL). The solution was refluxed for 6 h at the temperature of 75 °C, then poured into 500 mL water. The aqueous phase was extracted three times using EtOAc (3 × 50 mL), and the collected organic solution was dried over anhydrous sodium sulfate. After being concentrated, a colorless liquid was obtained. Yield: 16.8 g (94.4%). The product was used directly in the next step reaction.

**Preparation of 4-*n*-Butylstyrene.** The synthesis was performed according to literature<sup>19</sup> in a dried 250 mL 3-neck flask fitted with a reflux condenser and a nitrogen inlet. *p*-Toluenesulfonic acid (1.9 g, 10.0 mmol) was dissolved in dioxane (100 mL) and the solution was heated to 140 °C. The product of the last step, 1-(*n*-butylphenyl)ethyl alcohol (16.8 g, 94.0 mmol), was added dropwise. The reaction mixture was stirred for 2 h and poured into 500 mL water. The aqueous phase was extracted using EtOAc (3 × 50 mL). The collected organic layer was dried with anhydrous sodium sulfate. After being concentrated, the crude product was purified by silica flash chromatography with hexane mobile phase. A colorless liquid was obtained. Yield: 8.8 g (58.3%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 0.92 (t, 3H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.30 (m, 2H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.65 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.60 (t, 2H, Ar-CH<sub>2</sub>-CH<sub>2</sub>), 5.20, 5.70

(d, 2H, -CH=CH<sub>2</sub>), 6.70 (m, 1H, -CH=CH<sub>2</sub>), 7.15, 7.35 (d, 4H, -ArH-).

**Preparation of 1-Bromo-1-(4'-*n*-butylphenyl)ethene.** The synthesis was performed according to literature.<sup>20</sup> The bromination of 4-*n*-butylstyrene was conducted at 0 °C in CH<sub>2</sub>Cl<sub>2</sub>, yielding 1,2-dibromo-1-(4'-*n*-butylphenyl) ethane in high yields (~100%). A mixture of 1,2-dibromo-1-(4'-*n*-butylphenyl)ethane (32.0 g, 100.0 mmol), K<sub>2</sub>CO<sub>3</sub> (27.6 g, 200.0 mmol), THF (100 mL), and methanol (100 mL) was refluxed at 75 °C for 1 h. After cooled to room temperature, the mixture was extracted with hexane (3 × 50 mL) and washed with 300 mL saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate. After being concentrated, the crude product was purified by silica flash chromatography using hexane as the mobile phase. A colorless liquid was obtained. Yield: 17.4 g (72.8%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 0.93 (t, 3H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.35 (m, 2H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.60 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.60 (t, 2H, Ar-CH<sub>2</sub>-CH<sub>2</sub>), 5.70, 6.10 (d, 2H, -CBr=CH<sub>2</sub>), 7.15, 7.50 (d, 4H, -ArH-).

**Preparation of 2,3-di(*n*-Butylphenyl)-1,3-butadiene (1).** 1-Bromo-1-(4-*n*-butylphenyl)ethene (12.0 g, 50.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.57 g, 0.50 mmol), magnesium powder (0.60 g, 25.0 mmol) and THF (100 mL) were mixed in a 250 mL 3-neck flask fitted with a reflux condenser and a nitrogen inlet. The mixture was refluxed for 12 h and then cooled to room temperature. After addition of water (HPLC grade, 100 mL), the organic layer was extracted with ether (3 × 50 mL), and then dried over anhydrous sodium sulfate. The crude product was purified by silica gel column chromatography with hexane mobile phase. A colorless liquid was obtained. Yield: 3.0 g (37.6%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 0.90 (t, 6H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.35 (m, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.55 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.55 (t, 4H, Ar-CH<sub>2</sub>-CH<sub>2</sub>), 5.24, 5.52 (d, 4H, -C=CH<sub>2</sub>), 7.07, 7.31 (d, 8H, -ArH-). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 149.8, 142.3, 137.6, 128.3, 127.3, 115.4, 35.4, 33.6, 22.5, 14.0. FTIR: 2956, 2958, 2871, 2857, 1610, 1510, 1465, 898, 840. MS: *m/z* calcd for C<sub>24</sub>H<sub>30</sub> (M + H)<sup>+</sup>, 319; found, 319.

**Preparation of 2,3-Di(*tert*-butylphenyl)-1,3-butadiene (2).** The preparation of monomer 2 was similar to the preparation of 1 except that *tert*-butylbenzene was used in the reaction of acetylation. Yield: 65.3%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 1.30 (s, 18H, -C(CH<sub>3</sub>)<sub>3</sub>), 5.25, 5.55 (d, 4H, -C=CH<sub>2</sub>), 7.32, 7.36 (d, 8H, -ArH-). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 150.5, 149.5, 137.3, 127.0, 125.1, 115.5, 34.5, 31.33. FTIR: 2959, 2930, 2867, 1610, 1512, 1460, 1364, 1269, 904, 839. MS: *m/z* calcd for C<sub>24</sub>H<sub>30</sub> (M + H)<sup>+</sup>, 319; found, 319.



**Preparation of 2,3-Di(*n*-hexylphenyl)-1,3-butadiene (3).** The preparation of monomer 3 was similar to the preparation of 1 except that *n*-hexylbenzene was used in the reaction of acetylation. Yield: 57.7%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 0.90 (t, 6H,  $\text{CH}_2\text{---CH}_3$ ), 1.30 (m, 12H,  $\text{---CH}_2\text{---}(\text{CH}_2)_3\text{---CH}_3$ ), 1.60 (m, 4H,  $\text{---Ar---CH}_2\text{---CH}_2\text{---}$ ), 2.55 (t, 4H,  $\text{---Ar---CH}_2\text{---}$ ), 5.25, 5.55 (d, 4H,  $\text{---C=CH}_2$ ), 7.08, 7.34 (d, 8H,  $\text{---ArH---}$ ).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 149.8, 142.4, 137.6, 128.3, 127.3, 115.4, 35.7, 31.8, 31.4, 29.1, 22.7, 14.2. FTIR: 2956, 2926, 2855, 1610, 1510, 1465, 898, 854. MS:  $m/z$  calcd for  $\text{C}_{28}\text{H}_{38}$  ( $\text{M} + \text{H}$ ) $^+$ , 375; found, 375.

**Polymerization of 1.** All of anionic polymerizations were performed in Schlenk apparatus connected to vacuum/argon lines. The flask with a magnetic stir bar inside was dried by three cycles of flaming/Ar purging/evacuating and rinsed with a dilute solution of *n*-BuLi in cyclohexane, then pure cyclohexane, for several times. Monomer 1 was dried under high-vacuum condition for 24 h prior to polymerization. A volume of 50 mL of cyclohexane was distilled into the flask, and the impurities were titrated with DPELi (adduct of *s*-BuLi and 1,1-diphenylethylene) until red color appeared. Then THF (0.11 mL, 1.30 mmol) and 1 (1.00 g, 3.20 mmol) were added to form a solution. *s*-BuLi in cyclohexane/hexane (0.10 mL, 0.13 mmol) was added at 10 °C for 30 min, then the temperature was raised to 40 °C for 2 h. The polymerization was terminated with degassed methanol and the resulting polymer was precipitated from methanol and dried under vacuum for 24 h. Poly(1) $_{25}$  was obtained as white powder. Yield: 0.98 g (98.0%).  $M_{n,\text{GPC}} = 4.9 \times 10^3$  g/mol, PDI = 1.05,  $M_{w,\text{MALLS}} = 7.9 \times 10^3$  g/mol.

The preparation of poly(1) $_{50}$ , poly(1) $_{300}$ , poly(2) $_{30}$ , and poly(3) $_{25}$  were similar to the polymerization of poly(1) $_{25}$  except that the different monomers or amount were used. These results were presented in Supporting Information Table S3 and Figures S3–S12.

**Block Copolymerization.** Styrene was distilled over di-*n*-butylmagnesium ( $\text{MgBu}_2$ ) on the vacuum line prior to polymerization. The synthesis of poly(1)-*b*-polystyrene was conducted by sequential addition of two monomers in 40 °C. A volume of 50 mL of cyclohexane was distilled into the flask, and titrated with DPELi until a red color appeared. Then THF 0.11 mL (1.30 mmol) and monomer 1 (1.45 g, 4.55 mmol) were added to form a solution. *s*-BuLi in cyclohexane/hexane (0.10 mL, 0.13 mmol) was added at 10 °C for 30 min, then the temperature was raised to 40 °C for 2 h. Styrene (0.41 g, 3.9 mmol) was added at 10 °C, then the temperature was raised to 40 °C for 4 h. The polymerization was terminated with degassed methanol, and the product was precipitated in methanol and dried under vacuum for 24 h. Poly(1) $_{25}$ -*b*-polystyrene was obtained as white powder. Yield: 1.80 g (96.8%).  $M_{n,\text{GPC}} = 13.8 \times 10^3$  g/mol, PDI = 1.14.

**General Procedure for Bromination–Dehydrobromination.** A solution of bromine in dichloromethane (4.0 mmol, 3 mL) was added dropwise to a solution of poly(1) $_{25}$  solution in dichloromethane (0.64 g, 5 mL) at 0 °C. The mixture was stirred for 4 h and the product was precipitated into methanol and dried under vacuum for 24 h. Poly(1) $_{25}$ -Br was obtained as a greenish brown colored powder. Yield: 0.89 g (93.0%).  $M_{n,\text{GPC}} = 5.9 \times 10^3$  g/mol, PDI = 1.14.

The elimination of HBr was performed in THF solution at room temperature. A solution of potassium *tert*-butoxide in anhydrous THF (5.0 mmol, 5 mL) was added dropwise to a solution of Poly(1) $_{25}$ -Br in THF (0.30 g, 10 mL) under nitrogen. The mixture was stirred for 12 h and then dialyzed in deionized water and acetone, respectively, for 2 days and 4 h. The slurry in the bag was dissolved in THF and dried with anhydrous sodium sulfate. After evaporation of the solvent,  $\alpha$ -SPA(1) $_{25}$  was obtained as a dark brown powder. Yield: 0.16 g, 80.0%.  $M_{n,\text{GPC}} = 2.4 \times 10^3$  g/mol, PDI = 2.26 (high temperature GPC in 1,2,4-trichlorobenzene).

**General Procedure for the Dehydrogenation of Precursor Polymers with DDQ.** A powder of poly(1) $_{25}$  (0.32g, containing 1.00 mmol of butadiene units) was dried under vacuum in a 50 mL Schlenk tube. Toluene (3 mL) was added using a syringe, and the mixture was stirred until the polymer was completely dissolved. A solution of DDQ in toluene (0.91 g, 4.0 mmol, 3 mL) was added using a syringe. The mixture was stirred at 90 °C for 24 h, then poured into a large volume

of methanol to precipitate the polymer. After dried under vacuum for 24 h,  $\beta$ -SPA(1) $_{25}$  was obtained as a brown powder. Yield: 0.29 g (90.6%).  $M_{n,\text{GPC}} = 3.2 \times 10^3$  g/mol, PDI = 1.65 (high temperature GPC in 1,2,4-trichlorobenzene).

**Measurements.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out on a Bruker 500 and 400 MHz NMR instrument respectively, using  $\text{CDCl}_3$  as the solvent and tetramethylsilane as the interior reference. Gel permeation chromatography (GPC) analysis was performed through three TSK gel columns (pore size 15, 30, and 200 Å), calibrated by narrow polystyrene standards, and equipped with three detectors: a DAWN HELEOS (14–154°) (Wyatt multiangle laser light scattering detector, He–Ne 658.0 nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C.  $M_w$  was obtained by DAWN HELEOS in the online mode, with  $dn/dc$  values determined in Optilab rEX. UV spectra were recorded on a PerkinElmer Lambda 750 UV–visible spectrometer with a 1 cm $^2$  quartz cell. THF was used as the solvent. Element analysis of brominated polymers were carried out by oxygen flask combustion method or by XPS (for  $\alpha$ -SPAs) using PHI 5000C ESCA System. High temperature GPC were carried out on Agilent PL-GPC 220, using 1,2,4-trichlorobenzene as the eluent at a flow rate of 1.0 mL/min at 150 °C. Variant temperature NMR were performed on an Agilent Direct-Drive II 600 MHz spectrometer equipped with four broad-band rf channels and a 5 mm  $^1\text{H}$ – $^{19}\text{F}$ / $^{15}\text{N}$ – $^{31}\text{P}$  pulse field gradient (PFG) probe. The spectra in  $\text{C}_2\text{D}_2\text{Cl}_4$  was collected with a 1 s acquisition time, 3 s relaxation delay, 9.6 kHz spectral window, 256 transients, and 9.2  $\mu\text{s}$  90° pulse width. The data were exponentially weighted with a line broadening of 0.5 Hz.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Synthesis details, results of conventional and high temperature GPC,  $^1\text{H}$  NMR, and elemental analysis of concerned conjugated (co)polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*(J.H.) Telephone: +86-21-6564-3509. E-mail: [jphe@fudan.edu.cn](mailto:jphe@fudan.edu.cn).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We express thanks for the continuing financial support by the National Nature Science Foundation of China (21074024 & 21474016).

## ■ REFERENCES

- (1) (a) Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd ed.; CRC Press: Boca Raton, FL, 2007; p 20. (b) He, M.; Zhang, H.; Chen, W.; Dong, X. *Polymer Physics*, 2nd ed.; Fudan Press: Shanghai, PRC, 2006; p 26.
- (2) (a) Vogl, O.; Qin, M. F.; Zilkha, A. *Prog. Polym. Sci.* **1999**, *24*, 1481–1525. (b) Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4013–4022.
- (3) (a) Khlok, D.; Deslandes, Y.; Prud'homme, J. *Macromolecules* **1976**, *9*, 809–812. (b) Helbig, M.; Inoue, H.; Vogl, O. *J. Polym. Sci., Polym. Symp.* **1978**, *63*, 329–342. (c) Földes, E.; Deak, G.; Tüdös, F.; Vogl, O. *Eur. Polym. J.* **1993**, *29*, 321–330.
- (4) (a) Crawley, S.; McNeill, I. C. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2593–2606. (b) Kawaguchi, H.; Sumida, Y.; Muggee, J.; Vogl, O. *Polymer* **1982**, *23*, 1805–1814. (c) Kawaguchi, H.; Loeffler, P.; Vogl, O. *Polymer* **1985**, *26*, 1257–1264.
- (5) (a) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1345.

- (6) Ricci, G.; Lenoe, G. *Polyolefins J.* **2014**, *1*, 43–60.
- (7) (a) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51–56. (b) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, Z. *Prog. Polym. Sci.* **2001**, *26*, 721–798. (c) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745–754. (d) Liu, J. Z.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799–5867. (e) Masuda, T. Substituted Polyacetylenes. In *Conjugated Polymers: A Practical Guide to Synthesis*; Müllen, K., Reynolds, J. R., Masuda, T., Eds.; Royal Society of Chemistry: London, 2014; pp 37–60. (f) Li, S.; Liu, K.; Kuang, G.; Masuda, T.; Zhang, A. *Macromolecules* **2014**, *47*, 3288–3296. (g) Sakai, R.; Sakai, N.; Satoh, T.; Li, W.; Zhang, A.; Kakuchi, T. *Macromolecules* **2011**, *44*, 4249–4257.
- (8) (a) Ginsburg, E. J.; Gorman, C. B.; Marder, S. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 7621–7622. (b) Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397–1409.
- (9) Inoue, H.; Helbig, M.; Vogl, O. *Macromolecules* **1977**, *10*, 1331–1339.
- (10) Hirao, A.; Sakano, Y.; Takenaka, K.; Nakahama, S. *Macromolecules* **1998**, *31*, 9141–9145.
- (11) (a) Kanga, R. S.; Hogen-Esch, T. E.; Randrianalimanana, E.; Soum, A.; Fontanille, M. *Macromolecules* **1990**, *23*, 4241–4246. (b) Reibel, D.; Nuffer, R.; Mathis, C. *Macromolecules* **1992**, *25*, 7090–7095. (c) Leung, L. M.; Tan, K. H. *Macromolecules* **1993**, *26*, 4426–4436. (d) Bader, A.; Wunsch, J. R. *Macromolecules* **1995**, *28*, 3794–3800.
- (12) Luo, K.; Kim, J. S.; Cartwright, A. N.; Rzaev, J. *Macromolecules* **2011**, *44*, 4665–4671.
- (13) Ohashi, M.; Takeda, I.; Ikawa, M.; Ogoshi, S. *J. Am. Chem. Soc.* **2011**, *133*, 18018–18021.
- (14) (a) Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Symp.* **1980**, *67*, 43–71. (b) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497–2509.
- (15) (a) Shirakawa, H.; Sato, M.; Hamano, A.; Kawakami, S.; Soga, K.; Ikeda, S. *Macromolecules* **1980**, *13*, 457–459. (b) Soga, K.; Kawakami, S.; Shirakawa, H.; Ikeda, S. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 523–526.
- (16) (a) Tang, B.; Kong, X.; Wan, X.; Feng, X. *Macromolecules* **1997**, *30*, 5620–5628. (b) Kong, X.; Lam, J. W. Y.; Tang, B. *Macromolecules* **1999**, *32*, 1722–1730. (c) Kwak, G.; Masuda, T. *Macromolecules* **2000**, *33*, 6633–6635. (d) Lam, J. W. Y.; Dong, Y.; Cheuk, K. K. L.; Luo, J.; Xie, Z.; Kwok, H. S.; Mo, Z.; Tang, B. Z. *Macromolecules* **2002**, *35*, 1229–1240. (e) Yin, S.; Xu, H.; Su, X.; Li, G.; Song, Y.; Lam, J.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2346–2357.
- (17) (a) Kong, X.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **1999**, *32*, 1722–1730. (b) Percec, V.; Rudick, J. G.; Nombel, P.; Buchowicz, W. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3212–3220. (c) Percec, V.; Rudick, J. G. *Macromolecules* **2005**, *38*, 7241–7250.
- (18) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Part A: Polym. Chem.* **1975**, *13*, 1943–1950.
- (19) Quirk, R. P.; Ok, M. A. *Macromolecules* **2004**, *37*, 3976–3982.
- (20) Silveira, P. B.; Monteiro, A. L. *J. Mol. Catal. A* **2006**, *247*, 1–6.