ACS Macro Letters

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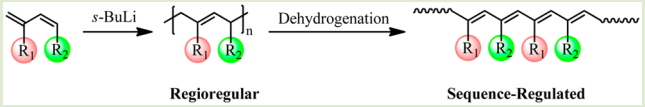
# Synthesis of Sequence-Regulated Polymers: Alternating Polyacetylene through Regioselective Anionic Polymerization of Butadiene Derivatives

Jia Li and Junpo He*

The State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

Supporting Information

**ABSTRACT:** We hereby report a strategy to synthesize sequence-regulated substituted polyacetylenes using living anionic polymerization of designed monomers, that is, 2,4-disubstituted butadienes. It is found that proper substituents, such as 2-isopropyl-4-phenyl, lead to nearly 100% 1,4-addition during the polymerization, thus, giving product with high regioregularity, precise molecular weight, and narrow molecular weight distribution. The product is convertible into sequence-regulated substituted polyacetylene by oxidative dehydrogenation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Block copolymers containing polyacetylene segment are also prepared. Owing to the versatility of the anionic reactions, the present strategy can serve as a powerful tool of precise control on polymer chain microstructure, architecture, and functionalities in the same time.




The precise control of macromolecular chain structure is a long-standing goal in the research of polymer chemistry. Various living or controlled polymerization techniques have been applied for the synthesis of polymers with well-defined molecular weights, molecular weight distributions, functionalities, and topological structures.[1−8] Nevertheless, the sequence control is a remaining challenge in polymer synthesis.[9−13]

Recently, there have been increasing efforts for the sequence control in polymer synthesis. A number of strategies were developed based on different chemistry or kinetic process. (1) The simplest case was the synthesis of alternating polymers, in which monomer pairs show strong tendency of cross-propagation. Such monomer pairs were, for instance, electron-rich and electron-deficient vinyl monomers in radical polymerization,[14−17] epoxides or aziridines and $CO/CO_2$,[18−20] epoxides and anhydrides,[21] alkene and CO,[22] and $\beta$-lactone pairs of opposite stereo center and with different substituents,[23] as well as isoprene and butadiene[24] in organometal-catalyzed polymerizations. In vinyl copolymerization, *d*-limonene and phenylmaleimide showed unique 1:2 copolymerization behavior, thus, giving copolymers with AAB sequence.[25] (2) A straightforward method to make sequence-regulated vinyl polymer was to perform each elementary propagation step in separate and successive way. This principle of "single monomer addition per step" was achieved in cationic oligomerization of vinyl ethers and styrenic monomer,[26] as well as in stepwise ATRA using allyl alcohol as the monomer precursor.[27] (3) For the synthesis of sequence-regulated condensation polymers, an iterative process of amidation and azide−alkyne click reaction in solution was developed to mimick the conventional step-by-step solid-phase approach of polypeptide synthesis.[28,29] (4) Polycondensation of designed monomers resulted in periodic copolymers with specific sequence segments arising from monomer structure. The polycondensation was based on thiol−ene addition reaction,[30] radical addition reaction between unconjugated C═C, and reactive C−Cl bonds,[31,32] as well as radical coupling either between carbon-centered radicals[33] or between carbon-centered and nitroxyl radicals.[34,35] (5) Multicomponent reactions, such as Passerini,[36,37] were utilized to make sequence-regulated poly(ester amide) with ordered side groups. (6) The sequence of the repeat unit could be incorporated into designed template monomers possessing multivinyl groups that polymerize through successive vinyl addition to form sequence-controlled polymers.[38,39] ROMP of cyclic template monomers bearing multifunctionalities in given order afforded polymers with corresponding sequence of the functionalities.[40] ADMET of acyclic $\alpha,\omega$-diene bearing a hydrocarbon side chain on specific position resulted in sequence-regulated polyethylene precursor.[41,42] (7) Sequence-regulated polymers could also be synthesized through kinetic control of the copolymerization process. Polymers with designed order and precise location of sparse functionalities were synthesized through a strategy of time-controlled addition of comonomers into living polymerization system of the main monomer. This strategy took the advantage of strong alternating tendency of electron-rich and electron-deficient monomers, such as styrene and maleimide derivatives.[43−52] In anionic polymerization, styrene, DPE and DPE derivatives were terpolymerized to form sequence-controlled terpolymers on the basis that DPE shows strong tendency to form alternating copolymers with styrene.[53] Sequence-controlled copolymetha-

**Received:** February 16, 2015
**Accepted:** March 13, 2015
**Published:** March 16, 2015



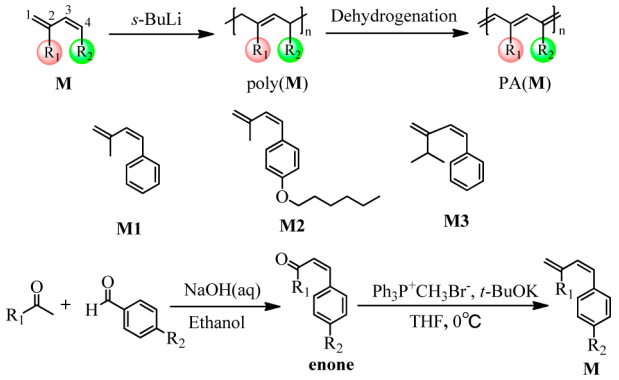


DOI: 10.1021/acsmacrolett.5b00125
*ACS Macro Lett.* 2015, 4, 372−376

crylates with gradient composition along the chain were synthesized in a one-pot strategy in which living radical polymerization and transesterification took place concurrently.[54] (8) A very unique insertion polymerization strategy was developed using styrene as monomer and a functional main chain containing multitrithiocarbonate as precursor. Under the reaction condition of RAFT, sequentially ordered polymer with specific spacing fragment between polystyrene segments in an alternating way was obtained.[55]

We hereby report a strategy to the synthesis of sequence-regulated polyacetylene, an important $\pi$-conjugated polymer, through living anionic polymerization of template monomers, 2,4-disubstituted 1,3-butadienes (carbon atoms are numbered in a way just for the convenience of discussion on reaction mechanism), followed by dehydrogenation (Scheme 1). One

**Scheme 1. Anionic Polymerization and Dehydrogenation of 2,4-Disubstituted Butadienes Made from Enones**




challenge of obtaining sequence-regulated polymerization products is to align the monomer addition into polymer chain in exclusive 1,4-style, and to avoid regio-isomerism, such as 1,2-, 3,4-, and 4,1-addition, which are usually encountered in conventional anionic polymerization. We achieve this regioregularity by monomer structure design placing asymmetric and bulky substituents at 2,4-position. Therefore, monomer addition at 1,2- and 3,4-position is prohibited due to steric hindrance, and monomer addition direction, 1,4- or 4,1, is controlled by different stabilizing effects of substituents at 2- and 4-position on the propogating carbanions.

Three kinds of butadiene monomers, **M1**−**M3**, with methyl or isopropyl at the 2-position, and phenyl or alkoxylphenyl at the 4-position, respectively, have been synthesized via enone intermediates followed by Wittig reaction (Scheme 1). The anionic polymerizations of these monomers are performed in THF, cyclohexane, or their mixture (THF/lithium = 10/1 molar ratio) using *sec*-BuLi as the initiator. The polymerizations give complete conversion in most cases, and the molecular weights of the products measured by light scattering are close to theoretical values (Supporting Information, Table S1). The chain microstructures of the products are analyzed using $^1$H NMR. The spectrum of poly(**M1**) shows signals at $\delta$ = 6.0 and 5.1 ppm, which are assigned to pendent vinylic and main chain olefinic protons, respectively. This demonstrates that both 1,2- and 1,4-enchainment are present in poly(**M1**)s synthesized from different solvents, and their relative contents depend on polymerization solvent (Figure S1). This result may indicate that the methyl group is not bulky enough to block the addition at 2-position. Interestingly, the addition style can be finely tuned by changing the electronic factor of the substituents. **M2** contains electron-donating hexyloxy on the phenyl ring, thus, disfavoring the formation of carbanion at the 4-position. Therefore, the content of 1,2-connection is even higher than that in poly(**M1**), as indicated by NMR results in Figure S2 and Table S1.

On the other hand, the spectra of poly(**M3**)s synthesized from different solvents show no signal at $\delta$ = 6.0 ppm, indicating the absence of 1,2-microstructure (Figure 1).

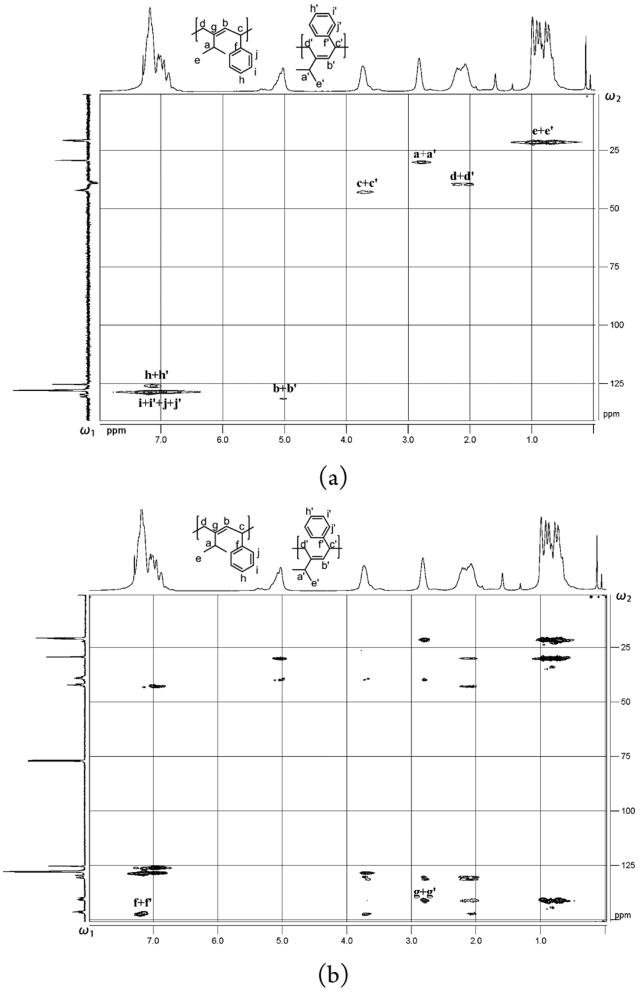



**Figure 1.** HSQC (a) and HMBC (b) spectra of poly(**M3**)$_{56}$ in $CDCl_3$.

Furthermore, the possibility of 3,4-addition can be excluded using $^{13}$C NMR by the absence of any signal in the range of $\delta$ = 100−120 ppm. If otherwise 3,4-addition takes place, the resulting pendent vinylic carbon would show signal in this range. Therefore, the enchainment of **M3** polymerization is nearly 100% 1,4-style. This is confirmed by the integration ratio of the signals of olefinic and isopropyl methine protons, 1:1. The two-dimensional NMR spectra in Figure 1, that is, heteronuclear singular quantum correlation (HSQC) and the heteronuclear multiple bond correlation (HMBC), exactly agree with the expected chain structure. Thus, it seems that isopropyl is more efficient than methyl in blocking the 2-position, leading to high selectivity in monomer addition manner. It is also noted that there are two peaks at $\delta$ = 3.2−4.0 ppm for main chain methine adjacent to phenyl group, which are assignable to *cis*/*trans* isomers.[56] The relative content of the



DOI: 10.1021/acsmacrolett.5b00125
*ACS Macro Lett.* 2015, 4, 372−376

configurational isomers depends on solvent property. THF gives high content of *cis* configuration (Figure S3).

Although there is no evidence to distinguish between 1,4- and 4,1-connection, it is believed that the polymerization proceeds in one directional 1,4-addition. This is because that the styrenic anion arising from 1,4-addition is much more stable, and much easier to form, than isopentyl anion arising from 4,1-addition.

The obtained poly(**M3**) is used as a precursor to make sequence-regulated polyacetylene, PA(**M3**), via 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)-catalyzed dehydrogenation.[57,58] The reaction is conducted in toluene at 60 °C for 12 h. During the reaction, the solution becomes dark brown and finally a brown colored powder is obtained after precipitation in methanol. The product is readily soluble in THF, toluene, DMF, acetone, and chloroform. $^1$H NMR in Figure 2 shows

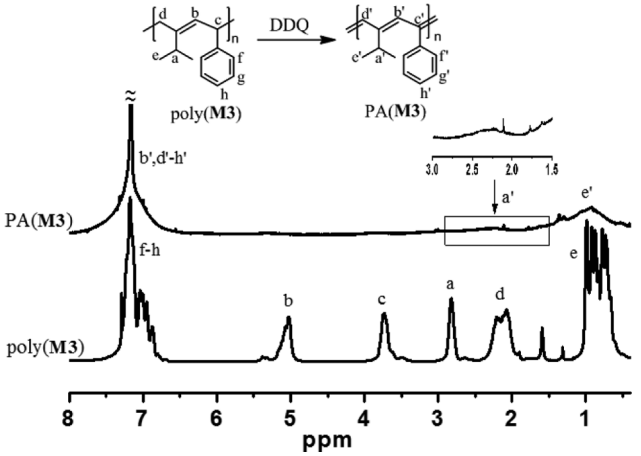



**Figure 2.** $^1$H NMR spectra of poly(**M3**)$_{56}$ in $CDCl_3$ and PA(**M3**)$_{56}$ in $C_6D_6$.

that, after dehydrogenation, the signals of main chain methylene (2.1 ppm) and methine (3.7 ppm) disappear, while the signal of the resulting olefinic protons and aromatic protons shift to the range of $\delta$ = 6.5−8.0 ppm to form a broad band.[59,60] The pendent isopropyl also gives broad absorption at around 2.2 ppm (methine) and 0.9 ppm (methyls) due to rigidity and configurational isomerism of the backbone.[61−63]

The UV spectra of poly(**M3**) and PA(**M3**) show that the latter gives absorption at wavelength longer than 350 nm, which is attributable to $\pi-\pi^*$ electronic transitions of the polyacetylene backbone (Figure S4).

GPC analysis indicates a living polymerization character for poly(**M3**) as it possesses expected molecular weight and narrow molecular weight distribution (Table 1 and Figures S5,6). However, PA(**M3**) displays very broad GPC profile, possibly due to aggregation behavior of the conjugated polymer. This broadening effect can be alleviated using high temperature GPC measurement.[64] The GPC trace of PA(**M3**) using 1,2,4-trichlorobenzene as the eluent at 135 °C show a unimodal main peak but remarkably reduced molecular weight and broad distribution (Figures S7−9). The reason(s) for the decrease in molecular weight may be due to oxidative cleavage during measurement under high temperature, strong interaction between polyacetylene, and the column packing material, as well as possible "cut-off" effect of rigid large molecular weight species by the column of high temperature GPC system.

The thermal stability of PA(**M3**) is similar to that of poly(phenylacetylene)[65] as measured by TGA. The start temperature of decomposition is around 250 °C and the residue is about 40% at 600 °C under nitrogen atmosphere. However, PA(**M3**) displays a two-stage weight loss profile, which is ascribed to the two kinds of repeat units with isopropyl and phenyl substituents in the alternating arrangement (Figure S10).

The present method can be applied for the synthesis of block copolymer containing PA segments. For instance, **M3** and styrene are block copolymerized in cylcohexane/THF mixed solvent (Scheme S1). The cross initiation goes well for both polystyrenyl anion and poly(**M3**) anion as the first block (Figure S11). The resulting block copolymers, PS-*b*-poly(**M3**) and poly(**M3**)-*b*-PS, are transformed into rod−coil block copolymers, PS-*b*-PA(**M3**) and PA(**M3**)-*b*-PS, respectively, under similar DDQ conditions (Figure S12). Nonetheless, block copolymer after dehydrogenation, such as PS-*b*-poly(**M3**), exhibits broad GPC curve with tailing effects to larger molecular weight region. Again, using high temperature GPC, narrower GPC curve with lower molecular weight is obtained (Figure S13). Another example is the synthesis of rod−rod block copolymers. In this case, block copolymerization of **M3** and 1,3-cyclohexadiene (CHD) is carried out in cyclohexane in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) (Scheme S2 and Table S3). The resulting block copolymer, polyCHD-*b*-poly(**M3**), containing 98% 1,4-units in polyCHD chain,[66] undergoes DDQ-catalyzed dehydrogenation at both segments and yields an all-conjugated block copolymer, poly(*para*-phenylene)-*b*-PA(**M3**) (Figures S14−16).

In conclusion, the first example of sequence-regulated substituted polyacetylene has been synthesized through living anionic polymerization of an asymmetric template monomer, 2-isopropyl-4-phenyl-1,3-butadiene, and the subsequent dehydrogenation in the presence of DDQ. The sequence-specificity is ensured by the regioselectivity during the polymerization.

**Table 1. Characterization Results of the Precursors and Corresponding Substituted Polyacetylenes**

| samples | solvent | temp. (°C) | time (h) | $M_{n,calc}$ (g/mol) | $M_{n,GPC}$ (g/mol) | $M_{p,GPC}$ (g/mol) | $M_{w,MALLS}$[a] (g/mol) | $PDI_{GPC}$ |
|---|---|---|---|---|---|---|---|---|
| poly(**M3**)$_{35}$ | CHX[b] | 50 | 6 | 5500 | 4100[c] | 4500[c] | 6000 | 1.06[c] |
| poly(**M3**)$_{53}$ | CHX/THF | 50 | 3 | 9600 | 6000[c] | 7400[c] | 9100 | 1.15[c] |
| poly(**M3**)$_{26}$ | THF | −50 | 1 | 5000 | 4500[c] | 5000[c] | 4500 | 1.07[c] |
| PA(**M3**)$_{26}$ | | | | 4950 | 2300[d] | 3600[d] | | 2.09[d] |
| poly(**M3**)$_{56}$ | THF | −50 | 2 | 11200 | 8200[c] | 9400[c] | 9700 | 1.08[c] |
| PA(**M3**)$_{56}$ | | | | 11100 | 4000[d] | 5500[d] | | 1.46[d] |
| poly(**M3**)$_{600}$ | THF | −50 | 3 | 101000 | 70100[c] | 90600[c] | 103000 | 1.18[c] |
| PA(**M3**)$_{600}$ | | | | 99800 | 5800[d] | 7500[d] | | 1.74[d] |

[a]Results of detector of multi angle laser light scattering. [b]Cyclohexane. [c]Results of conventional GPC. [d]Results of high temperature GPC.



DOI: 10.1021/acsmacrolett.5b00125
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Owing to the living feature of the polymerization and the controllability of chain microstructure through monomer design, the present synthetic strategy offers new opportunities for molecular engineering of polyacetylene-based homopolymers, block copolymers, and architectural copolymers.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: jphe@fudan.edu.cn.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the financial support by the National Natural Science Foundation of China (Grant No. 21474016). We are grateful to Junfang Li for the help in high temperature GPC measurement.

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DOI: 10.1021/acsmacrolett.5b00125
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DOI: 10.1021/acsmacrolett.5b00125
*ACS Macro Lett.* 2015, 4, 372−376