Synthesis of Isotope-Substituted Conjugated Ladder Polymers

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Abstract

Conjugated ladder polymers (cLPs) represent an intriguing class of macromolecules, characterized by their multi-stranded structure, with continuous fused π-conjugated rings forming the backbone. Isotope substitution, such as deuteration and carbon-13 labeling, offers unique approaches to address the significant challenges associated with elucidating the structure and solution phase dynamics of these polymers. For instance, selective deuteration can highlight parts of the polymer by controlling the scattering length density of specific molecular sections, thereby enhancing the contrast for neutron scattering experiments. In this context, deuteration of side-chains in cLPs represents a promising approach to uncover the elusive polymer physics properties of their backbone. The synthesis of two distinct types of cLPs with perdeuterated side-chains are reported here. During the synthesis, ^{13}C isotope labeling was also employed to verify the low defect levels of the synthesized polymers. Demonstrating these synthetic successes lays the foundation for rigorous characterization of the defects, conformation, and dynamics of cLPs.

1. Introduction

Ladder polymers represent a class of multi-strand macromolecules composed of an uninterrupted sequence of rings in the backbone, with adjacent rings sharing two or more atoms.[1] Conjugated ladder polymers (cLPs) are a distinct subtype of ladder polymers characterized by their continuous π-conjugation.[2,3] In contrast to traditional conjugated polymers, cLPs exhibit significantly greater backbone rigidity due to their unique structures.[1,4,5] Such backbone rigidity facilitates the delocalization of molecular orbitals and the fast transport of quasiparticles such as polarons and excitons along the backbone.[6-10] This contributes to the intriguing electronic and optical properties of cLPs and their promising applications in various types of electronic devices.[11-15] Additionally, many conjugated ladder polymers (cLPs) have demonstrated superior stability under harsh conditions or through numerous cycles of electrochemical transformations, owing to their thermodynamically stable yet kinetically persistent backbone constitution.[16-22]

Despite significant advances in the syntheses of cLPs, characterizing their chemical structures and physical properties remains challenging. Isotope substitution on the cLP macromolecules offers a promising technique for accurate characterization of this elusive class of polymers. For example, side-chain perdeuteration represents a promising method to probe the backbone conformation of cLPs in solution. Typically, the characterization of backbone conformation in cLPs by scattering techniques is complicated by the large volume of side-chains attached to the backbone for solubility.[5,23] If the side-chains of a polymer are perdeuterated, it is possible to probe the scattering signal of only the backbone when the polymer is dissolved in a deuterated solvent. This strategy has been proven to be efficient in aiding scattering studies in traditional non-ladder conjugated polymers across a wide range of rigidity.[24,25] However, deuterium labelling has not yet been widely utilized for cLPs due to synthetic challenges, thereby

hindering the investigation of backbone rigidity for cLPs. It is envisioned that deuteration can be selectively introduced into side-chains of cLPs, to enhance neutron scattering signal contrast, enabling precise structural and dynamic analyses.[26] For another example, carbon-13 (^{13}C) isotope labeling represents an important technique for characterizing potential structural defects in the multiple-stranded backbones of cLPs. This approach is particularly crucial for cLPs synthesized via the post-polymerization ladderization approach, where a non-quantitative cyclization reaction can lead to structural defects on the backbone.[1,3] These defects are typically challenging to quantify using conventional NMR spectroscopy due to the weak signal and broad peaks associated with cLPs. However, with highly enriched ^{13}C labeling at the key cyclization position, the resulting sharp ^{13}C NMR signal can be relied upon to characterize the outcomes of the ladderization process.[27-31]

Recognizing the importance of isotope substitution in characterizing cLPs, herein we report the syntheses of two different types of cLPs featuring perdeuterated alkyl side-chains. Meanwhile the successful ladderization of these polymers was confirmed by using ^{13}C labeling techniques. The synthesis of these cLPs sets the stage for neutron scattering measurements and other physical assessments of defect-free cLPs, thereby enhancing our understanding and utilization of these highly promising polymeric materials.

2. Results and discussion

2.1 Design of polymers

The flexibility of traditional conjugated polymers stems from the presence of single-bond linkages connecting conjugated rings along the polymer chains. This single stranded constitution allows the conjugated building blocks to rotate and/or bend around the single stranded C—C bond

with relatively low energy barriers.[4] As a result, depending on their backbone building blocks, conjugated polymers can behave from relative flexible chains to rigid-rod chains.[32] [33,3435] In contrast, cLPs have no rotatable sigma-sigma single bond along the backbone and consequently a highly planar backbone, thus its rigidity is expected to be quantitatively measured with the help from introduction of deuterium side-chains.[4,36]

In this study, two types of isotope-substituted cLPs (**P1** and **P2**, see **Figure 1**) were designed to feature perdeuterated side-chains as analogues of known ladder polymers.[19,27] Meanwhile, along the syntheses, ^{13}C substitution was introduced in order to probe the efficiency of the ladderization step and the defect level of the final ladder polymer product. The backbone of **P1** can be synthesized via a thermodynamically controlled reversible ring-closing olefin metathesis (RCM) reaction, which has been confirmed to afford a low defect level of the backbone.[27,37,38] The local rigidity of its ladder-type backbone was confirmed by photophysical analysis, while the extended rod-like structure was visualized under scanning tunneling microscope.[27] The backbone of **P2** is a ladder type analogue of polyaniline, which demonstrates the electrochemical switchability and electrical conductivity in the doped state similar to conventional polyaniline.[19] Meanwhile, such ladder type backbone exhibits excellent stability in operating electrochromic device.

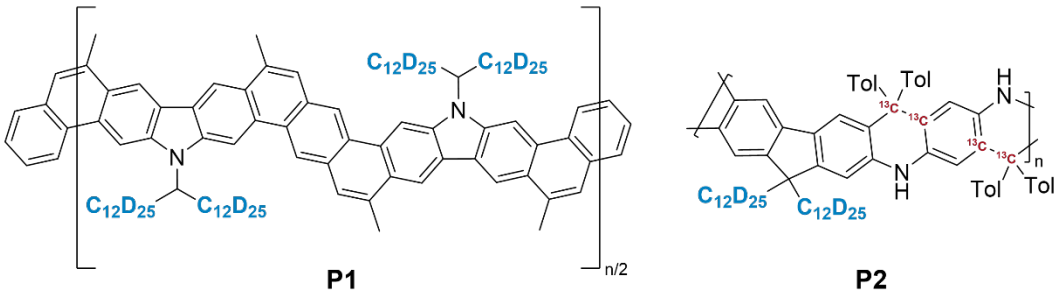

Figure 1. Structural formulas of **P1** and **P2**, with highlight on their deuterated side-chains (in blue color) and ^{13}C labeling.

For both **P1** and **P2**, the deuterated side-chain was synthesized starting from lauric acid $C_{11}H_{23}COOH$. Three rounds of Pt/C and Pd/C catalyzed hydrogen/deuterium (H/D) exchange reaction[4] were conducted in basic D_2O to afford perdeuterated lauric acid $C_{11}D_{23}COOD$. Subsequently, the carboxylic acid group was reduced by using lithium aluminum deuteride to give the perdeuterated alcohol $C_{12}D_{25}OD$ (**1**) (**Figure 2**). The three rounds of H/D exchange reactions ensured a high deuteration level, which was calculated to be > 96% (**Figure S6**). Subsequently, compound **1** was transformed into the bromide functionalized intermediate **2** (**Figure 2**), which was used as a common perdeuterated starting material for the synthesis of both cLPs **P1** and **P2**.

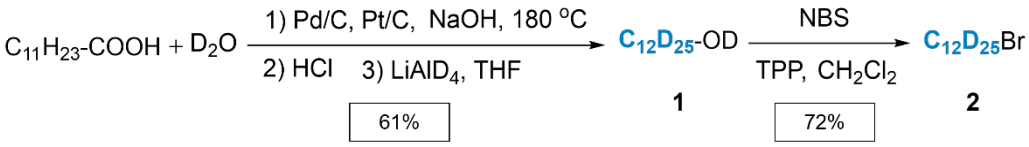

Figure 2. Synthetic scheme of perdeuterated starting materials $C_{12}D_{25}OD$ (**1**) and $C_{12}D_{25}Br$ (**2**).

Both **P1** and **P2** polymers are synthesized through an approach of polymerization followed by post-polymerization ladderization. It is crucial to ensure that the ladderization step takes place at a close to quantitative conversion, otherwise structural defects would present in the final cLP products. These defects can significantly influence the polymer's physical, optical, electronic properties, and durability. To verify the successful ring closing reaction, carbon atoms at or near the cyclizing functional groups were substituted by highly enriched ^{13}C isotope (> 98%) . This way, ^{13}C nuclear magnetic resonance (NMR) can be employed to assess the defect level. Despite that ^{13}C NMR is known to have a low sensitivity due to the low natural abundance of ^{13}C (~1%), ^{13}C NMR peaks of polymers are typically quite sharp in contrast to the typically very broad peaks observed in ^{1}H NMR. Here, the over 98% ^{13}C isotope labeling results in sharp and intense NMR peaks of these labeled positions, thereby enabling precise and sensitive defect characterization of the synthesized cLPs.

2.2 Synthesis of **P1**

The synthesis of cLP **P1** is outlined in **Figure 3**. α-branched perdeuterated side-chains were attached to the nitrogen center in the carbazole-derived repeating units of **P1**. In order to introduce this side-chain to the monomer starting material **M1 (Figure 3a)**, the synthesis began with reacting **2** with magnesium to form a Grignard reagent, $C_{12}D_{25}MgBr$. Two equivalents of $C_{12}D_{25}MgBr$ were then reacted with ethyl formate to give perdeuterated 13-pentacosanol. It was subsequently treated with 4-toluenesulfonyl chloride to give the perdeuterated side-chain intermediate **3**, which was subsequently attached to the nitrogen center of 2,7-dibromo-9H-carbazole via a nucleophilic substitution. The resulting product **4** underwent acetylation with acetyl chloride and subsequently a Wittig reaction, yielding the monomer **M1**. The presence of perdeuterated side-chains on **M1** was confirmed by the observation of C-D coupling on ^{13}C NMR spectra (**Figure 4a**, left) and mass spectrometry (**Figure S10**). It is noteworthy that the much larger mass of the perdeuterated alkyl chain rendered kinetically slower reactions in almost all the steps compared to those reported on non-deuterated analogue.[27,39] As a result, through these synthetic steps, either longer reaction time or higher temperature was needed in comparison to the reported procedures.[27]

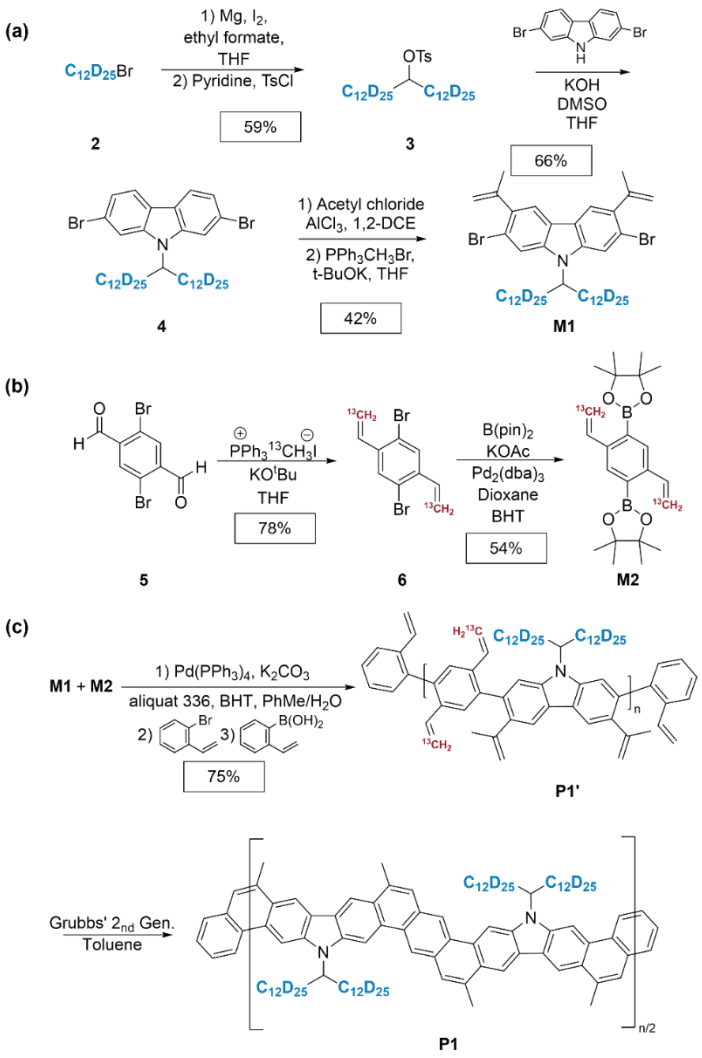

Figure 3. Synthetic scheme of (a) **M1**, (b) **M2**, and (c) **P1**.

^{13}C labeling was placed at the termini of the vinyl groups on the coupling partner monomer **M2 (Figure 3b)**. The synthesis of **M2** started with commercially available methyl-^{13}C-triphenylphosphonium iodide, which reacted with 2,5-dibromoterephthalaldehyde to give intermediate **6**. The bromide functional group on **6** was then converted into boron pinacolato via a palladium catalyzed Miyaura borylation reaction to afford **M2**. Successful synthesis of **M2** was demonstrated using ^{1}H NMR and mass spectrometry. The ^{13}C NMR spectra of **M2** revealed prominent peaks attributable to the ^{13}C labeling (**Figure 4a**, right).

To synthesize cLP **P1 (Figure 3c)**, **M1** and **M2** were mixed in a stoichiometric ratio and allowed to undergo a palladium catalyzed Suzuki coupling reaction, to give ^{13}C labeled precursor polymer **P1'** with perdeuterated side-chains. Size exclusion chromatography (SEC) analysis revealed M_n = 20.4 kg/mol and $Đ$ = 2.4. In its ^{13}C NMR spectrum, a high intensity peak at 114 ppm associated to the ^{13}C isotope labeled terminal vinyl carbon was observed (**Figure 4b**). RCM reaction was performed to ladderize **P1'** into the desired cLP **P1**. The thermodynamically driven RCM reaction provides a high conversion of the ladderization reaction as reported. This high conversion can be monitored by ^{13}C labeling on the functional groups participating in the RCM reaction by ^{13}C NMR efficiently. Specifically in **P1**, the terminal vinyl carbon was labeled by ^{13}C, so it would be totally removed in the RCM reaction to yield **P1**. As anticipation, the reaction affords **P1** with high conversion (24.0 kg/mol, $Đ$ = 1.4, by SEC) with no notable ^{13}C signal associated with the ^{13}C labeled terminal vinyl carbon, indicating the effective completion of the RCM reaction and extremely low level of defect in **P1**.

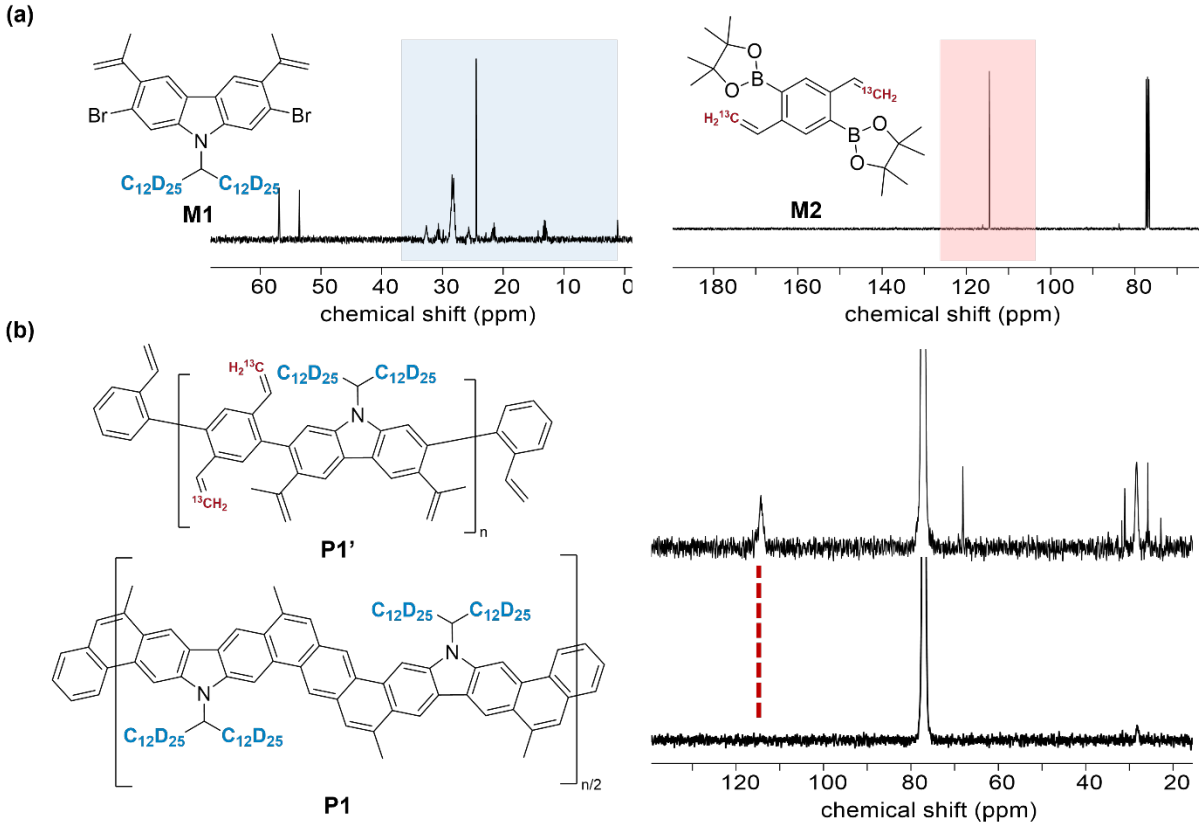

Figure 4. ^{13}C NMR spectra of (a) the monomer **M1** with deuterated side-chains (left), the monomer **M2** with ^{13}C labeling (right), in $CDCl_3$, 101 MHz, 298K. (b) **P1'** and **P1**, in $CDCl_3$, 126 MHz, at 298K.

2.3 Synthesis of **P2**

As outlined in **Figure 5**, **P2** was synthesized from fluorene derived monomer **M3**, on which two $C_{12}D_{25}$ side-chains are attached to the 9-position of the fluorene unit. The synthesis started with reacting compound **2** with 2,7-dibromofluorene under basic condition to afford **7 (Figure 5a)**. The two bromide groups were converted into two amino groups via a Buchwald-Hartwig reaction

with benzophenone imine, followed by hydrolysis to yield the monomer **M3**. Similar to **M1**, the deuterated side-chains on **M3** (**Figure a**, left) was characterized by the observation of C-D coupling on ^{13}C NMR spectra (**Figure S20**) and mass spectrum for **M3**. Similarly to the synthesis of **M1**, the introduction of deuterated side-chains extended the reaction time required for the conversion from **7** to **M3**.

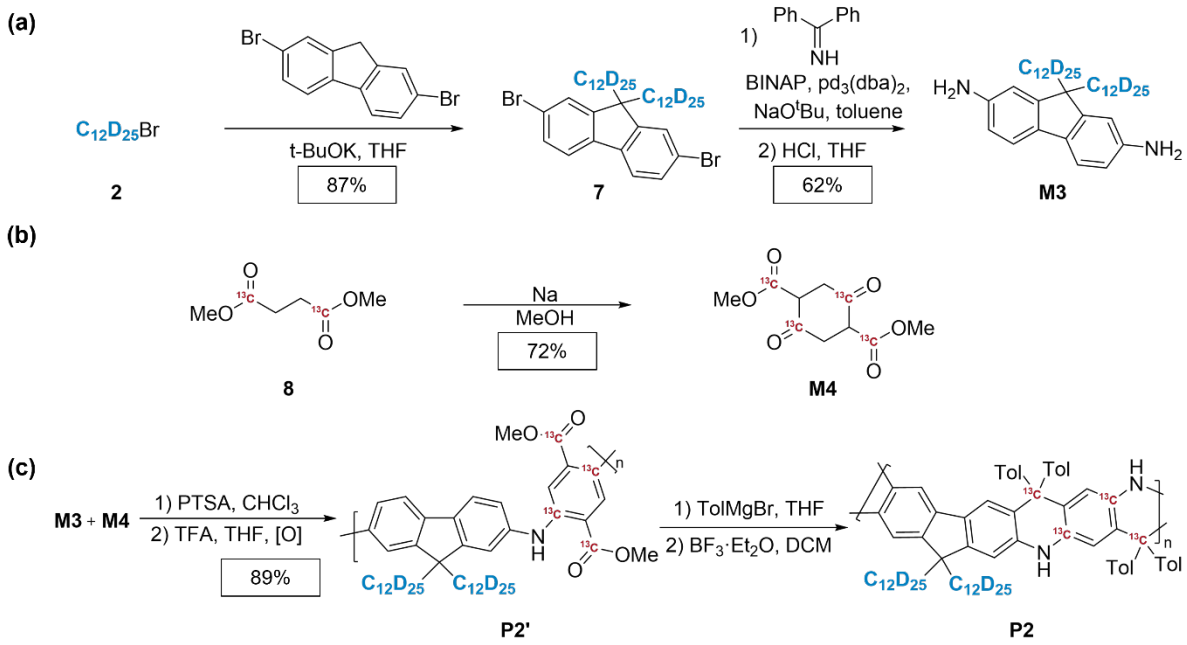

Figure 5. Synthesis of (a) **M3**, (b) **M4**, and (c) **P2**.

The coupling partner monomer **M4** was label with ^{13}C isotope in order to probe the possible defects during the synthesis of **P2**. Here, a commercially available starting material, dimethyl succinate-1,4-*$^{13}C2$* (**8**), was dimerized into dimethyl succinyl succinate, **M4**, with ^{13}C isotope labeling on all carbonyl carbon atoms (**Figure 5b**). To increase the yield in this cyclization reaction, sodium metal was directly mixed with methanol to produce sodium methoxide, which serves as the base to promote this reaction. Successful synthesis of **M4** was confirmed by using

^{1}H NMR (**Figure S21**) and mass spectrometry (**Figure S34**). ^{13}C labeling also gave prominent peaks on the ^{13}C NMR spectra of **M4** (**Figure**).

A palladium catalyzed Buchwald-Hartwig coupling polymerization was employed to polymerize **M3** and **M4**, to give **P2'** (M_n = 9.8 kg/mol, $Đ$ =1.4, by SEC). **P2'** underwent a Grignard reaction to convert all ester groups into di-*p*-tolyl substituted tertiary alcohol groups. Subsequently, a Lewis acid catalyzed ring closure reaction afforded the final cLP product **P2** (M_n = 10.2 kg/mol, $Đ$ = 1.4, by SEC), with the fluorene decorated with $C_{12}D_{25}$ side-chains (**Figure 5c**). ^{13}C labeling on the as (1) and (2) positions enables the precise monitoring during the ladderization reaction from **P2'** to **P2**. The clean shift of both ^{13}C NMR signals indicates the completion of the conversion. Specifically, position (1) on **P2'** shows a high-intensity peak at 168 ppm in the ^{13}C NMR spectrum. Following the ladderization process, this peak shifts to 57 ppm on **P2**, signaling the conversion of the carbonyl group on **P2'** to a sp^3 carbon on **P2**. Similarly, the ^{13}C labeled position (2) exhibits a shift from 138 ppm on **P2'** to 154 ppm on **P2**. The fact that no observable residual peaks at the original chemical shifts (168 and 138 ppm) in the ^{13}C NMR spectrum of **P2** indicates a high conversion of the desired cyclization during the ladderization process (**Figure 4b**). Furthermore, the absence of other peaks suggests that no undesired side reactions occurred during the process. These data suggested that the synthesized cLP **P2** has a well-defined backbone constitution with an extremely low level of defects that are not observed under ^{13}C NMR.

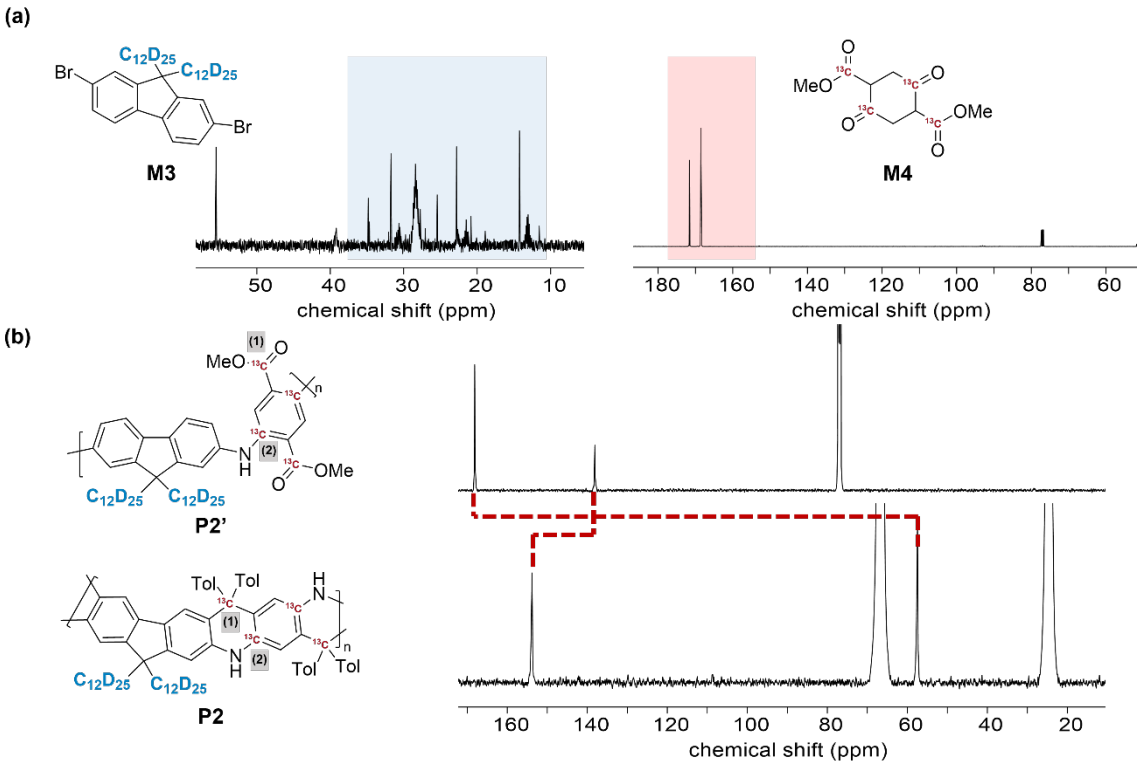

Figure 4. ^{13}C NMR spectra of (a) the monomer **M3** with deuterated side-chains (left), the monomer **M4** with ^{13}C labeling (right), in $CDCl_3$, 101 MHz, 298K. (b) **P2'** and **P1**, **P2'** are in $CDCl_3$, **P2** is in THF-d_6, at 298K.

Conclusion

In this study, we synthesized two isotope-substituted conjugated ladder polymers, P1 and P2, incorporating isotopic substituents such as deuterated side-chains and 13C labeling. The synthetic methodologies, building on previous research, were effective in incorporating deuterated side-chains into the ladder polymer backbone and constructing ladder polymer backbones with an extremely low level of defects. The demonstration of the feasibility of synthesizing well-defined conjugated ladder polymers featuring isotope substitution lays a solid foundation for future polymer physics studies of this underexplored class of polymers.

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