Post-polymerization modification of aromatic polyimides via Diels-Alder cycloaddition

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Abstract
We report a facile post-polymerization modification route to functionalized aromatic polyimides via Diels-Alder cycloaddition. Aromatic polyimides are important, versatile high-performance polymers; however, their structural diversity is restricted by the requirements of the step-growth polymerization. We prepared polyimides with alkynes in their main-chain as macromolecular dienophiles and quantitatively grafted tetraphenylcyclopentadienone based dienes. The resulting solution-processable, wholly aromatic polyimides show a considerable increase in surface area due to the induced conformational changes and bulky, rigid, and contorted molecular structures. The orthogonality of the reaction is exploited to insert functional groups, namely bromine and sulfonates, along the polymer backbone. In a further extension, the phenylene segments undergo cyclodehydrogenation to form nanographene segments within the polymer chains. The Diels-Alder cycloaddition onto polyimides is therefore demonstrated to be an effective, widely applicable route to tunable high-performance polymers with value-added functionality and thus considerable potential in a wide range of advanced materials.

KEYWORDS
Diels-Alder cycloadditions, nanographene, polyimides, polymers of intrinsic microporosity, polyphenylene, post-polymerization functionalization

1 | INTRODUCTION

The [4 + 2] Diels-Alder (D-A) cycloaddition reaction is a valuable tool in synthetic polymer chemistry.1 This atom efficient reaction can be performed without the use of catalysts, has an excellent functional group tolerance, and has been widely investigated for polymerization reactions.2,3 Indeed, the domino [4 + 2] cycloaddition reaction of di-alkynes with di-tetraphenylcyclopentadienones is an effective route to prepare fully aromatic polyphenylenes.4 This reaction involves an irreversible chelotropic evolution of CO gas at high-temperatures suppressing the retro-D-A reaction.5,6 Structural variations of the two components

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allow for the design of a variety of polymer architectures such as hyperbranched polyphenylenes,7,8 dendritic polymers,9–11 or block copolymers.12 Such conjugated macromolecular systems can be readily converted into graphene-like systems such as nanoribbons.13–17

Polyimides are established as one of the most important polymer materials for high-demand applications in electronics, aircraft, and space industries.18,19 Aromatic polyimides possess excellent thermomechanical performance, chemical, and radiation stability.18–21 The extended aromatic backbone results in high-chain rigidity, ultra-high glass transition temperatures \( T_g \) in the region from 250 to 400 °C and excellent mechanical properties over a high-temperature range.22–25 However, the structural diversity of aromatic polyimides is limited by the variety of available aromatic diamines and dianhydrides with suitable reactivity for the step-growth polymerization. While the D-A reaction has been used for synthesis of aromatic diamines and dianhydrides for polyimide synthesis,26,27 post polymerization functionalization offers a much more widely applicable method for introducing new functionalities to a polymer backbone.28,29

For polyimides, the most common approach to D-A post-polymerization modification is the incorporation of the maleimide group30 and the closely related nadimide group.31 These groups can be placed at one32 or both33 ends of a polymer chain or as pendant side chains30 and are used mainly for postprocessing modifications like crosslinking and molecular weight enhancement.34 Alkyne moieties have only sparingly been investigated for post-polymerization functionalization.29 Herein we investigate the use of the D-A reaction to create a toolbox to functionalize and manipulate the chemical structure of aromatic polyimides.

2 RESULTS AND DISCUSSION

The polydienophile PI-1a was prepared using the traditional two-step polyimide synthesis method as shown in Scheme 1 with the alkyne-containing anhydride 4. The first step involved the formation of the polyamic acid precursor solution followed by chemical imidization using acetic anhydride and pyridine. The 9,9'-bis (4-aminophenyl) fluorene 1 was selected as the diamine due to the bulky fluorene group which hinders chain packing, enhancing the polymer’s solubility. Subsequently, an excess of tetraphenylcyclopentadionene 5 was added to PI-1a and the reaction was stirred at 195 °C for 3 days in NMP. After precipitation and removal of the excess 5 by washing with EtOAc, the polymer PI-1b was characterized by SEC, NMR spectroscopy and FT-IR spectroscopy. According to the attached-proton-test, \(^{13}\text{C}-\text{APT-NMR} \) spectrum (Figure 1A) the conversion of the D-A reaction was quantitative, shown by the disappearance of the characteristic signal of the carbon triple bond at approximately 90 ppm. Additionally, an increase in the number of aromatic carbon signals was detectable after the reaction. The signals at 60 ppm and 166 ppm originating from the quaternary carbon of the diamine and the carbonyl group of the imide showed the chemical stability of the PI-1a backbone under the D-A reaction conditions. The preservation of the imide groups under the D-A reaction conditions was also confirmed by FT-IR spectroscopy (Figure 1B).

While alkyne moieties in polyimides are commonly applied for radical thermal crosslinking,19,35 this requires considerably higher temperatures in excess of 350 °C.36 The absence of crosslinking reactions in PI-1a at the D-A reaction temperature of 195 °C is demonstrated by the excellent solubility (in CHCl\(_3\), CH\(_2\)Cl\(_2\), and DMF) of polymer PI-1b. Furthermore, in DSC analysis of the PI-1b no exothermic peak for crosslinking could be observed after the D-A reaction, confirming the absence of alkyne moieties. In contrast, a clear exothermic curing peak was observed for PI-1a (Figure S1). The SEC chromatograms (Figure S2) showed that, despite an increase in molar mass, longer retention times were observed in the SEC elutionograms of starting material PI-1a \( (M_n \approx 46 \text{ kDa}) \), suggesting a considerable change in conformation (comparison of all SEC data in Table S1). The geometry of the backbone is altered at every site of functionalization, from the 180° bond angle of the CC=C bond to the 120° angle in the newly formed aromatic ring. Due to the conformational changes, we investigated the surface area (SA) by N\(_2\) physisorption isotherms (Table 1). Indeed, a significant increase in the apparent SA was observed upon D-A conversion.

Following these interesting results, we expanded the method to other polyimides, synthesizing PI-2a and PI-3a (Scheme 1), in order to explore the potential of the reaction to prepare high-surface area polyimides. For this purpose we prepared diamine 2 and the previously unreported 3, the latter exhibiting a contorted molecular structure due to its spiro carbon center. These additional kinks add rigidity to the polymer backbone and reduce packing efficiency. The additional rigidity and the steric hindrance from the methyl substituents further increase the rigidity of monomer 3 compared to 2. PI-2a and PI-3a then underwent the D-A conversion with 5 under the same conditions as PI-1a, yielding PI-2b and PI-3b respectively (Scheme 1). PI-2b and PI-3b were characterized by \(^{13}\text{C}-\text{NMR} \) spectroscopy with no signals being observed from the alkynes, indicating that the D-A reaction was again quantitative (Figure S39 and Figure S46). Both polymers (PI-2b and PI-3b) showed good solubility in common organic solvents such as CHCl\(_3\), CH\(_2\)Cl\(_2\) and
DMF. Interestingly, performing the D-A reaction on the DMF-insoluble PI-2a yielded the DMF soluble PI-2b (Figure S41). Analogous to the trend observed for PI-1a/1b, the SEC analysis showed a shift to longer retention times upon the D-A addition, again suggesting significant conformational changes (Figure S2).

As anticipated from the structural design, it was observed that PI-3a shows the highest apparent surface area due to the spiro structure of monomer 3 (Table 1). The surface area of PI-3a is an order of magnitude higher (Table 1) than the typical SA of polyimides, which are commonly in the range of 15–30 m² g⁻¹.³⁷ Furthermore, it was observed that the formation of hexaphenylbenzene moieties during the D-A reaction caused a significant increase in the apparent SA of these polyimides. The increase from PI-3a (with the highest starting SA) to PI-3b, is less pronounced but still significant. Such apparent BET surface areas in the range of 400 m² g⁻¹ are high for soluble polymers, although still somewhat lower than the best reported polymers of intrinsic micro-porosity (PIMs),³⁸,³⁹ which typically lie in the region of 600–800 m² g⁻¹.³⁷,⁴⁰,⁴¹ The calculation of the
contribution of micropores to the SA before the D-A reaction also has the highest value for PI-3a. The reason for this is the spiro carbon center increasing contortion along the polymer backbone. The relative simplicity and reproducibility of the post-polymerization D-A reaction means there is considerable potential for high-surface area microporous polymers to be attained with this chemistry in future generations.

The relative ease and orthogonality of these DA reactions facilitate the post-polymerization modification of polyimides with a broad range of functional groups. In order to demonstrate this capability, we introduced two different functional groups, namely bromine and sulfonate moieties (Scheme 2). The aryl bromide sites offer the potential for a wide variety of further functional groups, while such mechanically stable sulfonate-functionalized aromatic polymers are highly sought for as ion exchange membranes. We prepared compounds 6 and 7 and subsequently performed D-A reactions with PI-1a as the dienophile under the same conditions as mentioned above (NMP, 195 °C, 72 h). The polymers PI1-c and PI-1d were characterized with the same methods as the previously described polymers. No signals from the triple bonds are detectable in the 13CNMR spectra (Figure S53 and Figure S60), suggesting a complete conversion. Additionally, both polymers show good solubility in common organic solvents. PI-1c and PI-1d show both a decrease in the thermal stability, which can be attributed to the newly introduced functionalities (Figure S56 and Figure S63).

The presence of aromatic hexaphenylbenzene segments within the polyimide chains led us to inquire if cyclodehydrogenation is possible to convert them to polycyclic aromatic hydrocarbon (PAH) or “nanographene” segments. For this, PI-1b was treated under Scholl reaction conditions with AlCl3 and NaCl in the melt (Scheme 3). The resulting insoluble polymer PI-4 was then characterized via 2D solid-state NMR spectroscopy. As precise analysis and assignment of solid-state NMR spectra of such graphene-type molecules is challenging, we employed 1D and 2D NMR experiments in combination with state-of-the-art computational chemistry methods (Figure 2 and supporting information, section solid-state NMR data). The analysis confirmed the quantitative conversion to nanographene segments. This is an exciting proof-of-principle to prepare nanographene containing polyimides which, for example, could be extended in future work to

<table>
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<th></th>
<th>a S\text{BET prior D-A} [m^2 g^{-1}] (S_{micro} prior D-A [m^2 g^{-1}])</th>
<th>b S\text{BET after D-A} [m^2 g^{-1}] (S_{micro} after D-A [m^2 g^{-1}])</th>
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<tr>
<td>PI-1</td>
<td>8 (2)</td>
<td>137a (79)a</td>
</tr>
<tr>
<td>PI-2</td>
<td>57 (11)</td>
<td>250 (0)</td>
</tr>
<tr>
<td>PI-3</td>
<td>388 (180)</td>
<td>440 (200)</td>
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*Values estimated; see SI section PI-1b for more information.

**Table 1** BET surface area results and the calculated contribution of the micropores to the apparent surface area in brackets of PI-1, PI-2, and PI-3 before and after D-A reaction

**Scheme 2** Preparation of PI-1b, PI-1c, and PI-1d via D-A post-polymerization functionalization

**Scheme 3** Synthesis of PI-4 by cyclodehydrogenation reaction of PI-1b
fully soluble versions which open a host of possibilities in graphene-based electronics.

3 | CONCLUSION

In conclusion, we described a facile post-polymerization functionalization of polyimides through the Diels-Alder cycloaddition of tetraphenylcyclopentadienone to alkyne-based polydienophiles. The facile and effective modification strategy was confirmed to be quantitative by spectroscopic characterization. Interestingly, a significant increase in surface area was observed upon D-A functionalization, with apparent surface areas of over 400 m² g⁻¹ measured by BET, due to the bulky, rigid, contorted molecular structures. The wholly aromatic polyimides also had excellent solubility in common organic solvents. The reaction can be used as a molecular “toolbox” to add different functional groups due to the general orthogonality of the D-A reaction. We demonstrated this by the quantitative insertion of bromine and sulfonate groups along the polymer backbone. In a further extension, we demonstrate that the aromatic segments undergo cyclodehydrogenation to give “nanographene” segments within the polymer chains.

The post-polymerization Diels-Alder functionalization route is thus demonstrated to be a widely applicable route to solution-processable, thermally stable, high surface-area polyimides with value-added functionality. These novel high-performance polymers have considerable potential as future advanced materials, for example, as electron-transport materials or gas separation membranes.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.
REFERENCES


SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

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