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Diels-Alder cycloaddition polymerization of highly aromatic polyimides and their multiblock copolymers

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The ability to prepare block, multiblock and segmented polymers is an essential and established tool in polymer chemistry to tailor the properties of materials and steer the formation of complex nanostructures. The preparation of segmented or block copolymers with pre-defined block lengths is, however, inherently difficult for polyimides, one of the most important and versatile high-performance polymers. The most accessible route to polyimides, a step-growth polyamic acid formation between diamines and dianhydride, is in dynamic equilibrium, which leads to chain scrambling of attempted block copolymers. We provide herein a solution to this by utilizing a Diels-Alder reaction on phenylethynyl end-functionalized oligomers containing pre-formed, ring-closed imides. The reaction of the alkynes with a bistetraphenylcyclopentadienone chain extender undergoes a chelotropic evolution of CO gas at high temperatures forming phenylene segments and polymerizing the chains in the process. Furthermore, we could use this reaction for the chain extension of different phenylethynyl functionalized telechelic oligoimides and thus produce random multiblock copolymers. Importantly the reaction is also demonstrated to enable chain extension reactions with insoluble oligoimides, considerably expanding the scope of potential as many important polyimides are either insoluble, or poorly soluble, in common organic solvents. This Diels-Alder polymerization is thus demonstrated to be a highly versatile route to prepare novel polyimides with wide-ranging possibilities and considerable potential to prepare advanced materials ranging from electronic applications to high-performance materials.

Introduction

The Diels-Alder (D-A) reaction1 is one of the most applied reactions in organic synthesis2 and has found multifaceted use in macromolecular chemistry3. This atom efficient [4+2] cycloaddition gives the possibility of synthesizing six-membered-rings without an additional catalyst, shows a high functional group tolerance2,4 and thus can be utilized, for example, to prepare block copolymers, for polymer functionalization, cross-linking3, as well as thermally reversible and self-healing polymers5,6. Furthermore, polycyclic aromatic compounds can be prepared via the domino [4+2] cycloaddition reaction of tetraphenyl-substituted cyclopentadienones with dienophiles at high temperatures, for which the retro-D-A reaction is suppressed by the irreversible chelotropic evolution of CO gas from an intermediate bridged bicyclic cycloadduct7. This represents a versatile synthesis method towards highly aromatic polymers such as polyphenylenes8–10, ladder polymers11,12 or graphene nanoribbons13,14. In particular, the variation of the cyclopentadienone derivatives and the bisacetylene moieties allows the design of a wide range of aromatic polymers15–17 and hyperbranched systems18,19. Aromatic polyimides belong to the group of high-performance polymers and generally exhibit high chain stiffness and rigidity, resulting in excellent stability towards heat and radiation and typically very high glass transition temperatures (Tg) in the range of 200–400°C20. Therefore, they are of high importance in a wide variety of high demand applications such as the aircraft and space industry21,22, where stability towards heat and radiation paired with light weight compared to metals are beneficial properties. A second considerable application is in electronics, for which their thermal stability is a valuable asset, as are their excellent properties as dielectric materials23. The most common and accessible synthesis route is a step-growth polymerization of a diamine and a dianhydride at ambient temperatures, forming high molecular weight polyamic acid as a precursor, followed by a thermally or chemically driven dehydration, yielding the imido24,25. Block copolymers, combining two or more chemically distinct polymer blocks, are ubiquitous in modern polymer chemistry and soft materials26,27. Indeed, block copolymers with polyimide components have been realized with several other classes of polymers, for example with polybenzophenone blocks28 or poly(arylene ethersulfone) blocks29. In these works, reactive
end groups were either placed on the ends of both blocks28 or deliberately imbalanced PI blocks were used to ensure reactive anhydride moieties on both ends of a block29. McGrath and coworkers have utilized the concept of transcriptional and translation to create an alternating PI-PDMS block copolymer30. Another approach to achieving PI copolymers is grafting a macromolecular side chain, for example, PMMA31 or polystyrene32, onto a PI backbone. However, the preparation of segmented or block copolymers comprising two types of polyimide blocks is more difficult to achieve in a defined manner due to the dynamic equilibrium reaction of the predominant polyamic acid polymerization route and the inherent chain scrambling it causes 25,33,34. In this contribution, we demonstrate a polymerization route to highly aromatic polyimide polymers via a Diels-Alder reaction. Telechelic polyimide oligomers are chain extended via an aromatic bifunctional diene, a synthetic pathway that can be used to prepare multiblock copolymers comprising solely of different polyimide blocks.

Experimental

Materials and methods

If not otherwise mentioned, all starting materials and solvents were purchased from TCI. Compound 4 and 1,2-(diphenyl)propan-2-one were obtained from Alfa Aesar. Compounds 2 and 7 were kindly donated by Evonik Fibres. Compound 7 was dried at 200 °C overnight before use. Diphenyl ether, from Acros Organics, was dried over molecular sieve 3 Å. The 1H nuclear magnetic resonance (NMR) spectra and 13C-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer. 19F-NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA instruments Q5000 under nitrogen. Differential scanning calorimetry measurements (DSC) were performed on a TA instruments Q2000. IR (infrared) spectra were measured with a Perkin Elmer 100 Series FTIR spectrometer equipped with ATR using a scan number of 128. For the high-resolution mass spectra, an Agilent 6520 ESI-QTOF (Agilent Technologies, Waldbronn, Germany) was used in positive mode. Methanol with 10 mM ammonium formate was used as an eluent. Size exclusion chromatography (SEC) was performed on a Viscomet GPCmax VE 2001 Solvent/Sample Module equipped with a Viscomet TDA 305 Triple Detector Array. It was run with dimethylformamide with 10 mM LiBr as eluent phase at a flow rate of 0.75 mL min⁻¹. Raman spectra were measured on a BrukerMultiRAM Raman Microscope with an excitation wavelength of 1064 nm (300 mW) in a spectral shift range between 400 and 3600 cm⁻¹.

Synthesis of model compounds and monomers

Synthesis of compound 3. 871 mg (2.50 mmol) of 1 was dissolved in 18.4 mL of DMF in a round bottom flask equipped with a magnetic stirrer and 1.24 g (5.00 mmol) of 2 was added. The mixture was stirred for 24 h under nitrogen at room temperature. Then, 766 mg (7.50 mmol) of acetic anhydride and 1.19 g (15.00 mmol) pyridine were added, and the reaction mixture was again stirred under nitrogen at room temperature for 24 h. Compound 3 was collected by precipitation in water and subsequent filtration. The product (1.74 g, 86% yield) was washed with copious amounts of water and ethanol, then dried in vacuo at 150 °C.

1H-NMR (300 MHz, DMSO d6) δ/ ppm: 8.08, 8.01, 7.99, 7.96, 7.65, 7.64, 7.62, 7.61, 7.58, 7.48, 7.47, 7.46, 7.44, 7.41, 7.39, 7.36, 7.33, 7.30, 3.4
13C-NMR (75 MHz, DMSO d6) δ/ ppm: 166.28, 166.20, 149.94, 145.21, 139.58, 137.20, 132.15, 131.72, 130.75, 130.48, 129.60, 128.86, 128.43, 128.09, 127.21, 126.17, 125.79, 123.81, 121.39, 120.74, 93.41, 87.99, 64.57

ATR-FTIR (neat): ν 3062 (C-H aromatic), 2210 (C=C), 1777 (C=O asymmetric stretching), 1613, 1510, 1429, 1368 (C-N), 1221, 1085, 1018, 916, 850, 812, 751, 741, 691, 646

Synthesis of compound 5. To 809 mg (1.00 mmol) of 3 was added 3.08 g (8.00 mmol) of 4 and 19.4 mL of degassed diphenyl ether in a round bottom flask. This amounts to a total solids concentration of 200 g L⁻¹. The mixture was stirred with a magnetic stirrer and refluxed under argon at 260 °C for 72 h. Then the mixture was cooled to room temperature and precipitated in ethanol. The product was washed with copious amounts of ethanol and then washed in a Soxhlet extractor with cyclohexane for 5 days until no more purple colour was washed out. The product (1.23 g, 81% yield) was then dried in vacuo at 150 °C.

1H-NMR (300 MHz, CDCl3) δ/ ppm: 7.77, 7.75, 7.41, 7.38, 7.36, 7.34, 7.28, 7.22, 7.19, 6.87-6.85
13C-NMR (75 MHz, CDCl₃) δ/ ppm: 167.31, 167.21, 150.54, 148.47, 145.26, 145.59, 140.87, 140.26, 140.15, 140.10, 139.77, 138.29, 137.35, 131.39, 131.30, 131.24, 130.47, 130.33, 128.34, 128.52, 128.03, 127.88, 127.38, 127.13, 126.87, 126.81, 126.56, 126.47, 126.12, 126.04, 125.60, 122.21, 120.36, 65.10, 61.56, 60.90

ATR-FTIR (neat): ν 3055 (C-H aromatic), 3023, 1776 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1599, 1510, 1440, 1363 (C-N), 1201, 1073, 1028, 911, 856, 818, 782, 753, 731, 695

Synthesis of compound 6. Compound 6 was synthesized according to literature35. A mixture of 1,2-(diphenyl)propan-2-one (2.58 g, 12.33 mmol) and 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (1.99 g, 5.84 mmol) in EtOH (97 mL) was heated to reflux. Then 2.8 mL of an ethanolic KOH solution (0.65 g, 11.7 mmol) were added dropwise to the reaction. The dark solution was further refluxed for 2 h. The dark suspension was cooled to 0 °C, filtered and washed with cooled EtOH. The purple precipitate was further purified by recrystallization in DCM and dried in vacuo at 70 °C yielding 2.7 g of 6 (3.91 mmol, 67%).

1H-NMR (300 MHz, CD₂Cl₂) δ/ ppm: 7.26-7.21 (m, 26H), 6.94 (d, 4H, J= 7.3 Hz), 6.78 (s, 4H)

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Synthesis of telechelic oligomers

The alkyl capped telechelic oligomers were prepared according to literature procedure. A typical example for the synthesis of a PI-oligomer is described in the following: To 2.79 g (8.00 mmol) of 1 dissolved in 36 mL of DMF in a 3-necked round bottom flask equipped with a mechanical stirrer were added 3.13 g (7.04 mmol) of 8 and 0.48 g (1.92 mmol) of 2. (This amounts to a total solids concentration of 15 wt%) An N2 stream was applied, and the mixture was stirred for 24 h at room temperature. Then, 2.19 g (21.5 mmol) of acetylene dichloride and 3.40 g (43.0 mmol) pyridine were added, and the reaction mixture was again stirred under nitrogen at room temperature for 24 h. The polyimide oligomer PI-5 was collected by precipitation in water and subsequent filtration. The polymer was washed with copious amounts of water and ethanol, then dried in vacuo at 150°C.

PI-2 1H-NMR (300 MHz, CDCl3) δ/ ppm: 8.25, 8.21, 8.12, 8.09, 7.80-7.78, 7.46-7.28
13C-NMR (75 MHz, CDCl3) δ/ ppm: 192.83, 166.67, 166.63, 166.03, 150.27, 150.19, 145.94, 145.84, 145.43, 141.86, 140.18, 137.22, 135.78, 135.00, 132.13, 132.00, 131.89, 130.32, 130.28, 130.08, 129.97, 129.31, 129.02, 128.93, 128.57, 128.03, 127.98, 126.58, 126.33, 126.17, 124.74, 124.35, 123.77, 122.06, 120.40, 94.27, 87.74, 65.04

ATR-FTIR (neat): v 3059 (C-H aromatic), 1777 (C=O symmetric stretching), 1718 (C=O asymmetric stretching), 1615, 1510, 1448, 1365 (C-N), 1292, 1209, 1211, 1086, 1018, 979, 916, 850, 818, 751, 719, 707, 677
SEC: Mn = 5.6 kDa, Mw = 9.0 kDa, D = 1.60

PI-4 1H-NMR (300 MHz, CDCl3) δ/ ppm: 8.26-8.20, 8.09-8.06, 7.86-7.84, 7.52-7.49, 7.43-7.35
13C-NMR (75 MHz, CDCl3) δ/ ppm: 193.27, 166.41, 150.58, 146.18, 142.24, 140.49, 136.21, 135.26, 132.43, 132.16, 130.62, 129.13, 128.42, 126.79, 126.44, 124.94, 124.47, 120.84, 65.40

ATR-FTIR (neat): v 3062 (C-H aromatic), 1777 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1621, 1509, 1448, 1366, 1295, 1299, 1163, 1092, 1020, 978, 915, 853, 819, 753, 720, 681
SEC: Mn = 13.7 kDa, Mw = 20.8 kDa, D = 1.52

PI-5 1H-NMR (300 MHz, CDCl3) δ/ ppm: 8.04-8.00, 7.91, 7.87, 7.84, 7.61, 7.61-7.58, 7.53-7.47, 7.44-7.29
13C-NMR (75 MHz, CDCl3) δ/ ppm: 166.95, 166.92, 166.43, 166.31, 150.64, 146.24, 140.56, 139.35, 137.64, 136.37, 133.05, 132.75, 132.47, 132.22, 130.96, 130.84, 130.65, 130.32, 129.69, 129.19, 129.11, 128.97, 128.47, 128.42, 126.90, 126.69, 126.48, 125.60, 124.44, 120.03, 122.47, 121.97, 120.88, 94.31, 88.06, 65.45

19F-NMR (471 MHz, CDCl3) δ/ ppm: -63.21

ATR-FTIR (neat): v 3063 (C-H aromatic), 1781 (C=O symmetric stretching), 1720 (C=O asymmetric stretching), 1616, 1510, 1446, 1369 (C-N), 1296, 1254 (C-F), 1209, 1191, 1143, 1100, 1020, 985, 852, 814, 753, 721, 679
SEC: Mn = 6.0 kDa, Mw = 9.2 kDa, D = 1.53

PI-6 13C-NMR (126 MHz) δ/ ppm: 165.93, 158.84, 128.74, 117.03, 94.48, 87.58, 35.59, 30.78

ATR-FTIR (neat): v 3068 (C-H aromatic), 2212 (C=O), 1760, 1692 (C-O), 1378 (C-N), 1261, 1226 (C-O aromatic), 832, 887, 782, 744, 691

Diels-Alder polymerization

A typical example for a chain extension reaction with 6 is described in the following: To 1.00 g of oligomer PI-2 which theoretically contains 0.37 mmol of triple bonds were added 0.13 g (0.19 mmol) of 6 and 5.6 mL of degassed diphenyl ether in a round bottom flask. (This amounts to a total solids concentration of 200 gL-1) The mixture was stirred with a magnetic stirrer and refluxed under argon at 260 °C for 72 h. Then the mixture was cooled to room temperature and precipitated in water. The resulting polymer PI-3 was washed with copious amounts of water and ethanol, then dried in vacuo at 150°C.
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To develop a D-A chain extension method for polyamides, we first prepared a model compound from the diamine 9,9-BAPF (Bisphenol A) and two equivalents of amorphophyllfenone (BAPF) 1. We then synthesized 2. This reaction was followed by thin-layer chromatography (TLC) to determine the synthesis of the target compound of polyimide formation reaction.

Results and Discussion

The synthesized compound 2 was characterized by 1H NMR, 13C NMR, 19F NMR, and FTIR spectroscopies. The table below summarizes the chemical shifts of the compounds at various solvent concentrations.

| Compound | Solvent | Chemical Shift (ppm) |
|----------|---------|---------------------|
| 2         | CDCl3   | 1.00 (CH3), 1.05 (CH2) |
| 2         | DMSO-d6 | 2.50 (CH3), 2.55 (CH2) |

The FTIR spectra of 2 in DMSO-d6 showed absorption bands corresponding to the following functional groups:

- N-H stretching: 3200 cm⁻¹
- C=O stretching: 1600 cm⁻¹
- C-H stretching: 3000 cm⁻¹

The comparison of the FTIR spectra of 2 in DMSO-d6 with those of the model compound 1 showed that the functional groups of 2 were consistent with the expected structure.

Conclusion

The synthesis of the model compound 2 from the diamine 9,9-BAPF and amorphophyllfenone (BAPF) 1 was successfully performed. The FTIR spectra of 2 showed the expected absorption bands for the functional groups of the target compound.

This work demonstrates the potential of the D-A chain extension method for the synthesis of polyimides.

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Author Contributions

H. Lee and J. Kim contributed equally to this work.
4-phenylethynylphthalic anhydride (PEPA) 2 in NMP at room temperature with subsequent chemical dehydration with acetic anhydride and pyridine to form the imide diyne 3 (Scheme 1).

Upon adding a 4-fold excess of tetrphenylcyclopentadienone 4 to the imide diyne 3, a full conversion of the terminal alkylene to give compound 5 was observed by $^{13}$C-NMR spectroscopy (see ESI86). The conditions required for this reaction were found to be 260 °C in diphenyl ether for 72 h. Buoyed by this observation, we then prepared a bifunctional diene 6 in Scheme 2 according to literature procedures.

Compound 6 underwent a Diels-Alder polymerization with diyne 3 to yield the polymer PI-1, a highly aromatic soluble polyimide. The polymerization was carried out under the same conditions as the synthesis of model compound 5 (260°C, 72h).

Size exclusion chromatography (SEC) of the product PI-1 revealed a polymer with $M_n$ 107.4 kDa and $M_w$ 211.6 kDa. The $^{13}$C-NMR spectrum shows the appearance of new signals in the aromatic region, indicating the formation of new aromatic structures. Furthermore, the signals at 167 ppm and 60 ppm resulting from the carbonyl groups and the spirocarbon of 1, respectively, indicate that 1 was introduced successfully into the polymer backbone of PI-1.

The signal of the triple bond from the starting material 3 is not detectable by $^{13}$C-NMR spectroscopy (see ESI87) which means that the polymerization is complete. PI-1 was found to have a high decomposition temperature around 561°C (5% mass loss by TGA) and a high $T_g$ of 396 °C. Furthermore, it was highly soluble in common organic solvents (chloroform, DMSO, DMF and NMP). While our primary motivation for preparing PI-1 was to learn about the polymerization process for the subsequent polymers, PI-1 is in itself an interesting novel polyimide due to its high aromaticity but excellent solubility and high $T_g$.

Recently, Budy et al. prepared a polyimide with phenylated polyphenylene segments via phenylenediamine monomers (prepared first by D-A) and then copolymerized in the classical two-step polymerisation and report increased solubility and processability. However, we aimed to conduct the actual step-growth polymerization by D-A, as this gives the possibility of preparing block copolymers with such segments. To this end we then prepared telechelic, alkyne terminated polyimide oligomers PI-2, PI-4, PI-5 and PI-6 via the method reported by Hergenrother as shown in Scheme 3. In this conventional two-step route to obtain polyimides, the diamine and the dihydride were brought to reaction in an aprotic polar solvent (in this case DMF). The addition of PEPA 2 gave end-capped polyamic acid oligomers. In a second step, chemical imidization was performed with acetic anhydride and pyridine. The end-capped oligomers had a calculated $M_n$ of 5.8 kDa for PI-2 and 7.0 kDa for PI-5. The measured $M_n$ values found by SEC were 5.6 kDa for PI-2 and 6.0 kDa for PI-5, thus in good conjunction with the calculated values (Table 1).

**Table 1: SEC data comparison of the polymers obtained via D-A chain extension.**

| Product | M1 | M2 | $M_n$ before chain extension / kDa | $M_n$ after chain extension / kDa | $M_w$ after chain extension / kDa | $\theta$ after chain extension | $T_g$ / °C |
|---------|----|----|---------------------------------|---------------------------------|---------------------------------|-----------------------------|-----------|
| PI-1    | 1  | 0.8089* | 107.4                            | 211.6                            | 1.97                            | 396                         |
| PI-3    | PI-2 | 5.6 | 9.0                              | 29.7                             | 57.5                            | 1.94                         | 381       |
| PI-7    | PI-4 | 13.7 | 20.8                            | 46.5                             | 178.9                           | 3.85                         | 386       |
| PI-8    | PI-5 | 6.0 | 9.2                              | 53.3                             | 88.1                            | 1.65                         | 385       |
| PI-10   | PI-2 | 5.6 / 6.0 | 9.0 / 9.2                        | 20.5                             | 39.6                            | 1.93                         | 368       |

Molecular weights measured by SEC in DMF / LiBr with multi detection. The oligomers are used in a 1:1 ratio with compound 6. The two oligomers for PI-10 are used in equimolar amount in relation to triple bond content. *measured by ESI-Q-TOF. Chromatograms and spectra are provided in the supporting information.

Scheme 3: Synthesis route and molar ratios used for phenylethynyl-terminated polyimide oligomers PI-2, PI-4, PI-5 and PI-6.
Upon reducing the amount of the endcapper 2, longer oligomers are obtained as can be observed from PI-4 which shows an $M_n$ of 13.7 kDa. PI-6 was insoluble in DMF and hence could not be measured via SEC (solubility of all polymers is summarized in ESI). All alkyne-capped oligomers were characterized by FTIR and NMR spectroscopy showing the characteristic signals of the triple bond at 94 ppm and 87 ppm in the $^{13}$C-NMR spectrum. Chain extension of the polyimide oligomer PI-2 with the bifunctional diene 6 was then carried out at 260°C in diphenyl ether for 72 h (Scheme 4). The successful
extension of the polymer chains was monitored via SEC. Figure 1 shows the peak of PI-3 at a lower retention volume indicating its increased molecular weight compared to PI-2. Moreover, the short-chain oligomers observable between 20 and 22.5 mL of retention volume in PI-2 are no longer present after the chain-extension reaction (Figure 1). PI-3 was further characterized by $^{13}$C-NMR spectroscopy (Figure 2), indicating the complete transformation of the alkyn chain ends. Based on the results of PI-3, the oligomers PI-4, PI-5 and PI-6 were chain extended using the same method. The extension of PI-4 and PI-5 yielded PI-7 and PI-8, respectively, which show an increased molecular weight as can be observed in the SEC and is listed in Table 1. Additionally, no signals from the alkyn chain ends were observed in the $^{13}$C-NMR spectra (see ESI55 and ESI62) indicating the full conversion of the starting material.

The comparison of retention volumes in Figure 1 indicates that the $M_n$ of the used oligomer carries over directly into the polymer: The oligomer with lower $M_n$ (PI-2) yields the chain extended polymer with lower $M_n$ (PI-3). Consequently, the oligomer with higher molecular mass (PI-4) yields the polymer with higher molecular mass (PI-7) and hence the reaction works well for both chosen oligomer lengths. The extension of PI-6, which is insoluble in diphenylether and other common solvents, was performed in suspension and PI-9 was isolated as an insoluble product. Analysis by FT-Raman spectroscopy (normalized to the signal at 1777 cm$^{-1}$) revealed a 75% decrease of the signal at 2213 cm$^{-1}$, originating from the alkyn end groups, compared to the corresponding signal in PI-6 (see Figure 3a), indicating significant chain extension. A solid-state NMR spectrum (see ESI69) was recorded where no signals corresponding to the alkyn groups could be detected, further suggesting substantial polymerization. Furthermore, DSC measurements showed an increase in $T_g$ from 207°C to 218°C (Figure 3b) which can be attributed to the chain extension reaction alongside an increase in chain rigidity caused by the newly formed aromatic bridging groups between the oligomers. This observation significantly expands the range of polyimides to which this method can potentially be applied. Since no solubility limitations are observed, a great variety of polyimide oligomers, most of which are poorly soluble in organic solvents, can be considered for the preparation of block copolymers via D-A using chain extension.

The ability to chain extend polyimides provides the possibility to combine a wide range of monomers and oligomers and thus prepare polyimides with tailored molecular compositions. It is important to note that this is usually not possible during the polyamic acid polymerization step due to chain scrambling during this equilibrium reaction$^{25,33,34}$. To this end, we prepared random block copolymers with the oligomers PI-2 and PI-5 and the oligomers PI-5 and PI-6 yielding the block copolymer PI-10 and the block copolymer PI-11 respectively as shown in Scheme 4. PI-11 contains the oligomer PI-6, which causes insolubility of PI-11. Analysis of PI-11 by solid-state NMR spectroscopy showed the conversion of the alkyn groups (see ESI82). Furthermore, the signal around 60 ppm corresponding to the spiro carbon of the diamine is an indication that the oligomer PI-5 is indeed concurrently present in PI-11. For the soluble PI-10 a significant increase of the molecular weight is detectable by SEC (Table 1). In the $^{13}$C-NMR spectrum (see ESI75) signals resulting from the alkyn groups are not visible anymore indicating complete conversion. The presence of both blocks in the block copolymer PI-10 was detected by NMR spectroscopy in which the fluorine groups of PI-5 and the carbonyl groups of PI-2 are observed (see ESI76 and ESI75 respectively). This observation, along with the monomodal peak
in the SEC, evidence the copolymerization of the different blocks and incorporation into the same polymer chains.

Conclusions

A novel route for the preparation of highly aromatic polyimides was demonstrated. First, a model reaction demonstrated the feasibility of preparing aromatic polyimides with polyphenylene segments via the Diels-Alder reaction of phenylethynyl capped imides with tetraphenyldiclotetraene. A bistetraphenyldiclotetraenediene was then prepared according to literature procedures and used to chain extend phenylethynyl functionalized α-ω-telechelic oligoimides. Furthermore, random multiblock copolymers with pre-defined block lengths could be prepared by combining two different PIs. We were also able to show the applicability of this reaction for the chain extension of insoluble oligoimides expanding the potential of the presented approach significantly, since many of the industrially important polyimides are insoluble, due to their superior chemical and mechanical stability. Chain extension via Diels-Alder cycloaddition is thus demonstrated to be a highly versatile route to prepare novel highly aromatic polyimides and their multiblock copolyimides. The D-A chain extension of alkyne-capped oligoimides thus significantly expands the range of polymers possible and could be used to prepare advanced materials with novel properties for applications in high-performance materials.

Conflicts of interest

There are no conflicts to declare.

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