RESEARCH ARTICLE

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Macromolecular Chemistry and Physics
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Solution Self-Assembly of Branched Macromolecules Obtained via Iterative OPE Synthesis and the Passerini Three-Component Reaction

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In the last decade, isocyanide-based multicomponent reactions, like the Passerini three-component reaction (P-3CR), have gained significant interest in the synthesis of sequence-defined macromolecules due to their high efficiency and straightforward one-pot procedures. The P-3CR results in unique product structures that are particularly interesting for the synthesis of uniform, branched macromolecules, as they enable the direct introduction of a new branching point into the molecule. In this work, the synthesis of uniform first-generation dendrons is performed via the P-3CR using a divergent approach, utilizing three uniform and poorly soluble oligo(phenylene ethynylene)s (OPEs) of varying lengths as a focal moiety. Self-assembly of the dendrons in cyclohexane solution is confirmed by fluorescence spectroscopy and diffusion-ordered NMR (DOSY NMR) spectroscopy, highlighting the utility of DOSY NMR spectroscopy for the investigation of solution self-assembly. Diffusion coefficients for the dendrons and their aggregates are determined and compared for different lengths of the OPE focal moiety. The successful synthesis of the dendrons in good yields and the selective branching introduced on the OPEs by the P-3CR emphasize the high efficiency and synthetic advantages of multicomponent reactions for the preparation of uniform, branched macromolecules.

1. Introduction

One of the most important and fascinating basics of life is the highly defined structure of biopolymers such as DNA, RNA, proteins, or peptides. The dependence of these biopolymers' properties on the exact placement of structurally diverse monomers implements a broad variety of possible functions.[1] The importance of sequence-definition ($Đ$ = 1.00) in biological systems is thus emphasized by the effect of the specific arrangement of their building blocks on their 3D structures.[2,3] In contrast to the highly ordered, aperiodic structures of biopolymers, classic polymer science was dominated by uncontrolled copolymers with dispersities higher than $Đ$ = 1.00 for a long time.[4] However, the highly ordered and defined structure of biomacromolecules inspired chemists to investigate the preparation of sequence-defined synthetic macromolecules.[5] Currently, sequence-defined macromolecules in the range of oligomers can be precisely prepared using several different approaches.[6,7] Oligomers are, according to the definition of IUPAC, molecules whose properties change significantly with the addition of monomer units.[8] Thus, sequence-defined, uniform oligomers are particularly interesting for the investigation of structure-property relationships and allow fine-tuning for specific applications.[8–10]

Among many uniform macromolecules, oligo(phenylene ethynylene)s (OPEs) gained significant interest, as they are extensively π-conjugated, stiff oligomers that are suitable for applications as molecular wires,[11–17] in biosensing,[18,19] or photovoltaics[20] as well as for optoelectronic applications,[21–23] because of their highly fluorescent nature and molecular conductance.[16,18,24] Sequence-defined OPEs can be synthesized using different iterative synthesis approaches. Divergent/convergent and bidirectional approaches, combinatorial linear synthesis, and synthesis of OPEs on soluble and solid support have been reported by different authors.[25–35]

A recent approach for the synthesis of uniform OPEs, published by Meier et al. in 2021, exploits a carboxylic acid moiety as one of the key functional groups for a two-step iterative cycle (decarboxylative coupling, saponification) yielding sequence-defined OPEs.[36] This is particularly interesting, as these

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DOI: 10.1002/macp.202300337

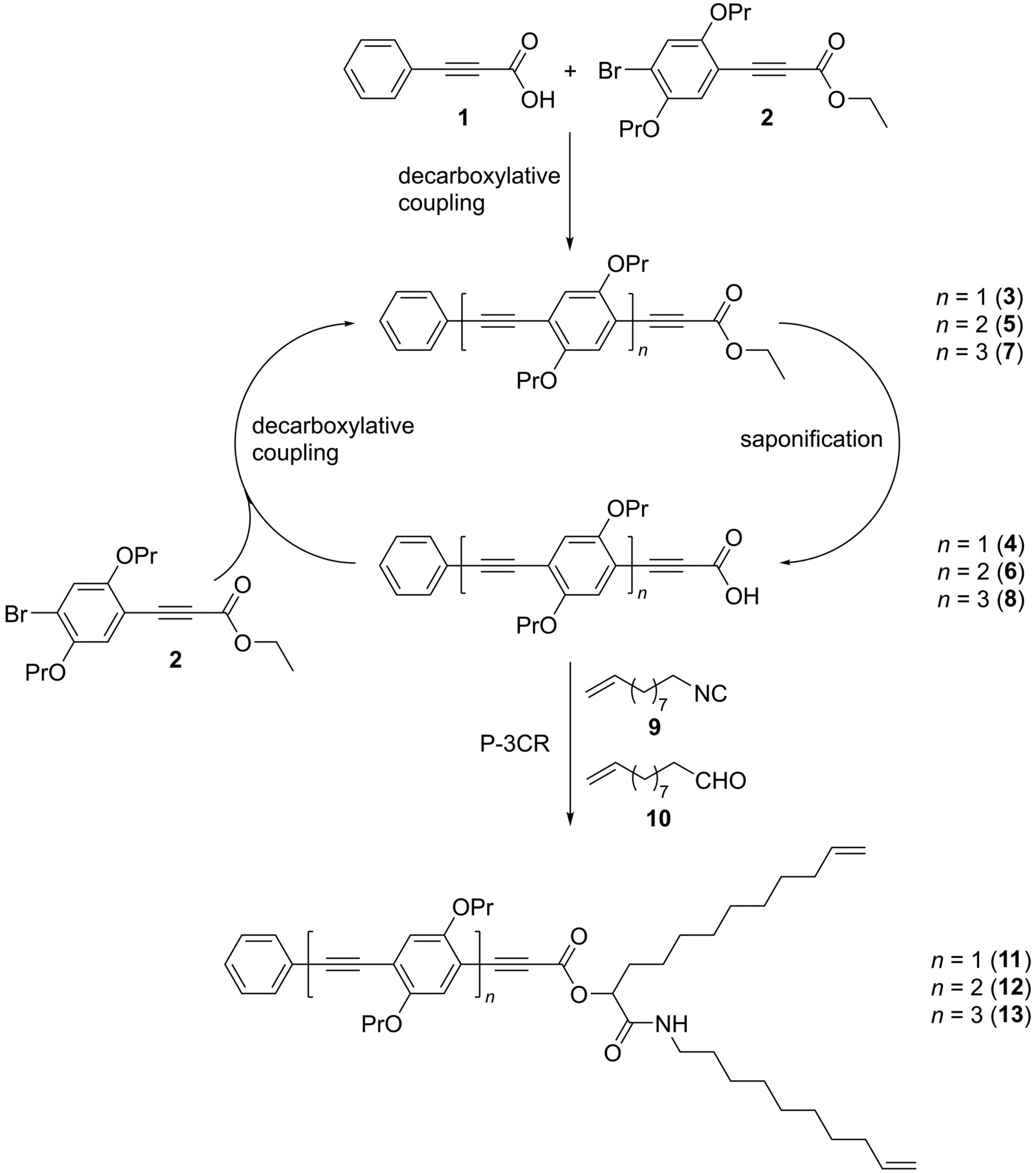

Figure 1. Synthesis procedure toward uniform dendrons bearing OPEs as focal moieties. The synthesis of the uniform OPEs is performed using an iterative cycle of decarboxylative coupling and saponification reported by Meier et al. in 2021.[36] Passerini reaction on the saponified OPEs results in uniform first-generation dendrons having an OPE as focal moiety.

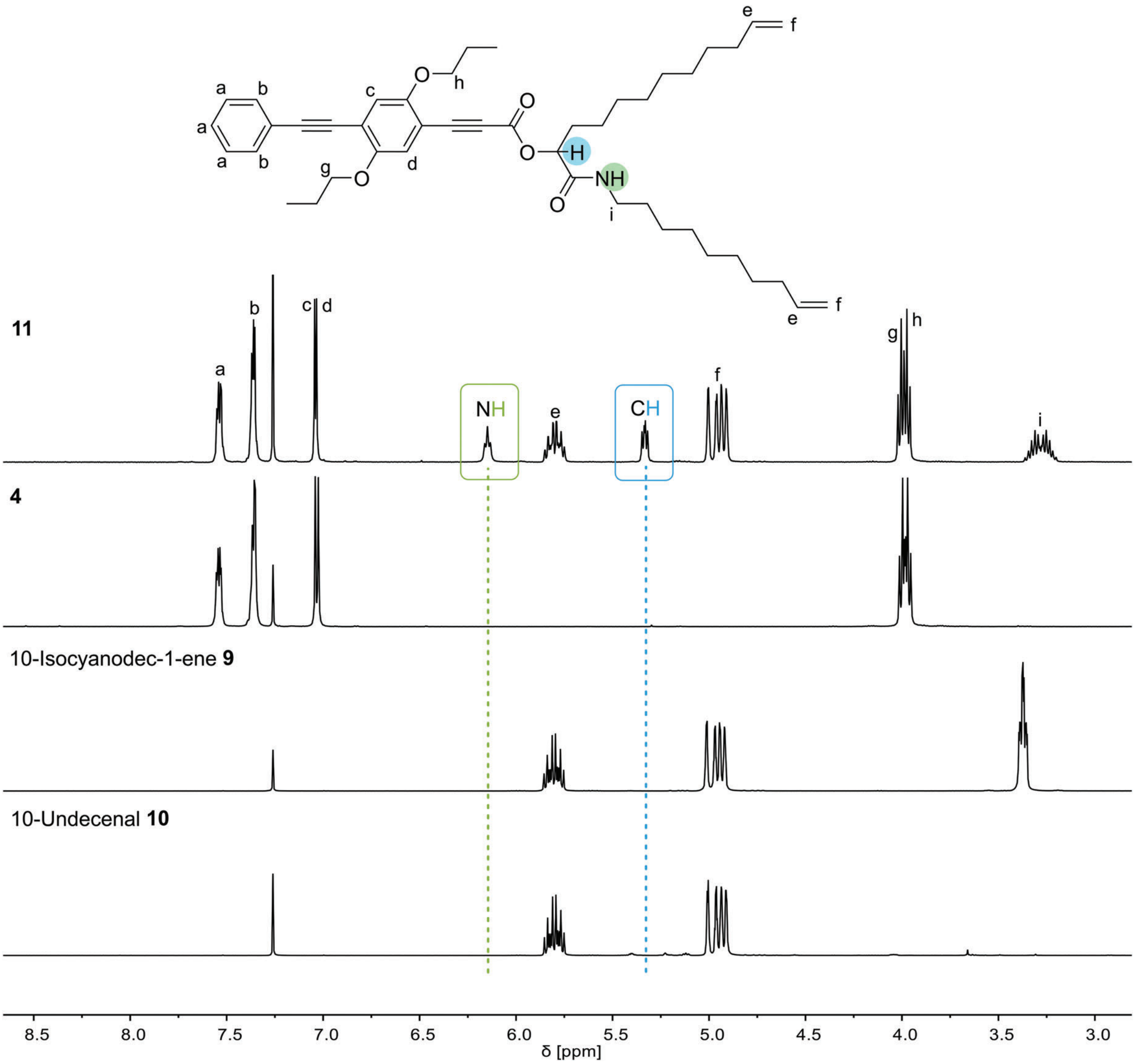

Figure 2. Comparison of ^{1}H NMR spectra of 11,4,10-isocyanodec-1-ene (9) and 10-undecenal (10) in $CDCl_3$. The emerging signals of the amide NH proton and the CH proton indicate the formation of the Passerini product (green and blue lines, respectively).

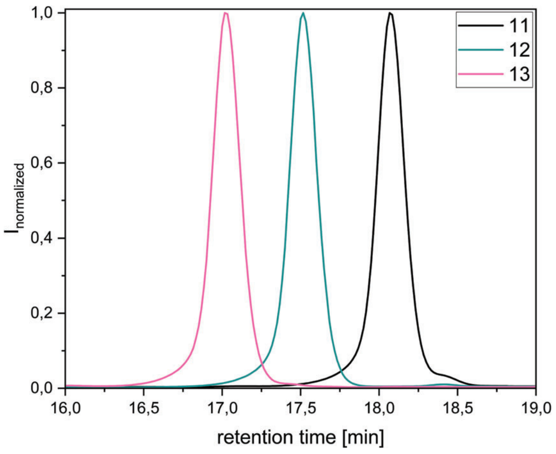

Figure 3. SEC curve of 11 (pink), 12 (green), and 13 (black) in THF. The determined dispersity for all three dendrons is Đ = 1.00.

carboxylic acid functionalized OPEs were already shown to be suitable as carboxylic acid components in a Passerini three-component reaction (P-3CR).[37] Since multicomponent reactions like the P-3CR are by now well-established tools for the preparation of uniform macromolecules,[38–48] the synthesis of OPEs using a decarboxylative coupling approach offers many possibilities for further modification of the OPEs, such as the introduction of dendritic scaffolds.

Table 1. Molecular weights and dispersity of dendrons 11, 12 and 13, determined by SEC in THF.

Dendron	M_n [kDa]	M_w [kDa]	$Đ$
11	1.31	1.31	1.00
12	1.68	1.69	1.00
13	2.12	2.13	1.00

Since dendrimers and dendrons are usually prepared in an iterative manner, they also belong to the class of uniform macromolecules.[49] However, there are only a few published examples of the synthesis of dendrimers via the P-3CR.[41,42,50,51] Thus, it can be interesting to combine uniform OPE moieties with dendrons via the P-3CR to obtain block-like oligomers, depicting the properties of both structural motifs. Especially if both structural motifs exhibit different properties, such as different solubilities, it can be interesting to investigate the self-assembly of such macromolecules in solution. Since OPEs are rather hardly soluble molecules, the introduction of well-soluble branched architectures on the OPEs may cause self-assembly of the OPE dendrons in a suitable solvent. It is expected that in solution, the OPEs aggregate as poorly soluble moiety, while the well soluble branched architectures point toward the solvent medium. Diffusion-ordered NMR (DOSY NMR) spectroscopy is a 2D NMR method that allows NMR signals to be assigned to a diffusion coefficient. It can be used, for example, as a method to determine the purity of a compound or to assign NMR signals to compounds in a complex mixture.[52–56] Moreover, it was shown to be a suitable tool for the investigation of self-assembly to supramolecular structures.[57–61]

In this work, we present the divergent synthesis of dendrons using uniform OPEs of different lengths as focal moieties by applying the P-3CR as a branching reaction, using the OPEs as carboxylic acid component (**Figure 1**). Additionally, the self-assembly properties of the synthesized and fully characterized dendrons were investigated via fluorescence spectroscopy as well as DOSY NMR spectroscopy. The shown results emphasize the applicability and value of DOSY NMR spectroscopy for the analysis of the self-assembly in solution.

2. Results and Discussion

2.1. Synthesis of First-Generation Dendrons

Three first-generation dendrons were synthesized, bearing uniform OPEs with one to three repeating units as a focal moiety. These OPEs were prepared using an iterative decarboxylative coupling approach reported by Meier et al. in 2021[36] (see Supporting Information for characterization), as this route advantageously offers a carboxylic acid moiety on one end of the OPEs, which can then act as a carboxylic acid component for a P-3CR without further modification of the OPE. Using these carboxylic acid end-groups, 10-isocyanodec-1-ene and 10-undecenal were introduced as branching reagents via a P-3CR.

By this synthesis approach (Figure 1), three first-generation dendrons bearing defined OPEs of different lengths were prepared and isolated in good yields (71–87%). The structure and purity of all intermediate products were confirmed by NMR spectroscopy, IR spectroscopy, and MS, as shown in the Supporting Information. The formation of the Passerini product after OPE synthesis was confirmed via NMR spectroscopy. The emerging signals in the ^{1}H NMR spectrum of **11** at 6.15 and 5.33 ppm can be assigned to the NH proton of the amide group and the CH proton between the ester group and the amide group, respectively. **Figure 2** compares, exemplarily, the ^{1}H NMR spectra of **4**, **9**, **10**, and the final dendron **11**, confirming the success of the synthesis. ^{1}H NMR spectra of **12** and **13** showed the same characteristics (see Figures S3 and S5, Supporting Information). SEC analysis showed symmetric, narrow, and monomodal curves, confirming that uniform dendrons ($Đ$ = 1.00, **Figure 3**) were obtained. As expected, the retention time increased with decreasing length of the OPE focal moiety. The molecular weight and dispersity of each dendron are shown in **Table 1**. When looking closely at the SEC traces of **11** and **12**, a small peak at a retention time of ≈18.4 min is observable. To exclude residues of unconverted OPEs or other possible building blocks and side products, ESI-MS was performed for all three dendrons. By ESI-MS, no proton, sodium, or potassium adducts of **1**, **2**, **3**, **4**, **5**, **6**, **9**, or **10** or other possible impurities were found. Thus, the peak seen in the SEC traces of **11** and **12** could not be assigned. For **12**, an SEC purity of 98.8% was determined via integration. However, for **11** an SEC purity could not be determined, as the small peak is overlapping with the main peak.

2.2. Self-Assembly of First-Generation Dendrons in Cyclohexane

To investigate potential self-assembly of the synthesized macromolecules in solution, fluorescence spectroscopy, and DOSY NMR spectroscopy were chosen as analytical methods. All self-assembly investigations were performed in cyclohexane as a medium, as OPEs are not well soluble in cyclohexane, while the aliphatic chains are. Thus, the difference in solubility of the focal moiety and peripheral segment should lead to the formation of aggregates. Other solvents were not applicable, as either both structural motifs of the molecule were (partly) soluble or both parts were insoluble. Thus, a driving force for the self-assembly would not have been present.

Fluorescence spectra were recorded for different concentrations of **11** in cyclohexane (0.2–1 mM). All samples were excited at 365 nm and the emission was detected between 380 and 700 nm. The fluorescence spectra for the measured concentrations of **11** in cyclohexane are depicted in **Figure 4**.

Regarding the fluorescence spectra of **11** at different concentrations, a non-linear increase in fluorescence intensity can be

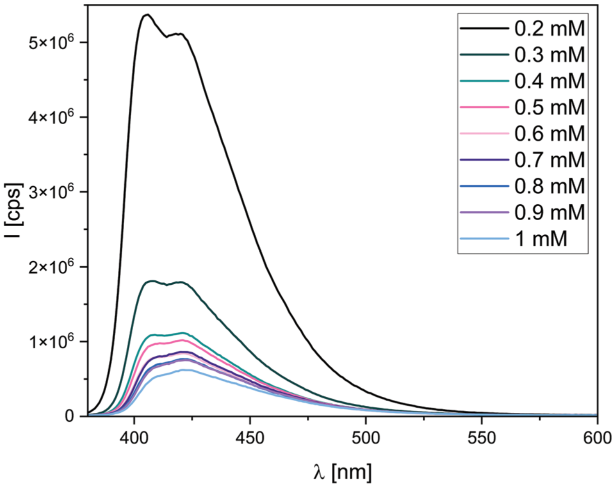

Figure 4. Fluorescence spectra of different concentrations of 11 in cyclohexane. All samples were excited at 365 nm and the emission was detected in the range of 380–700 nm.

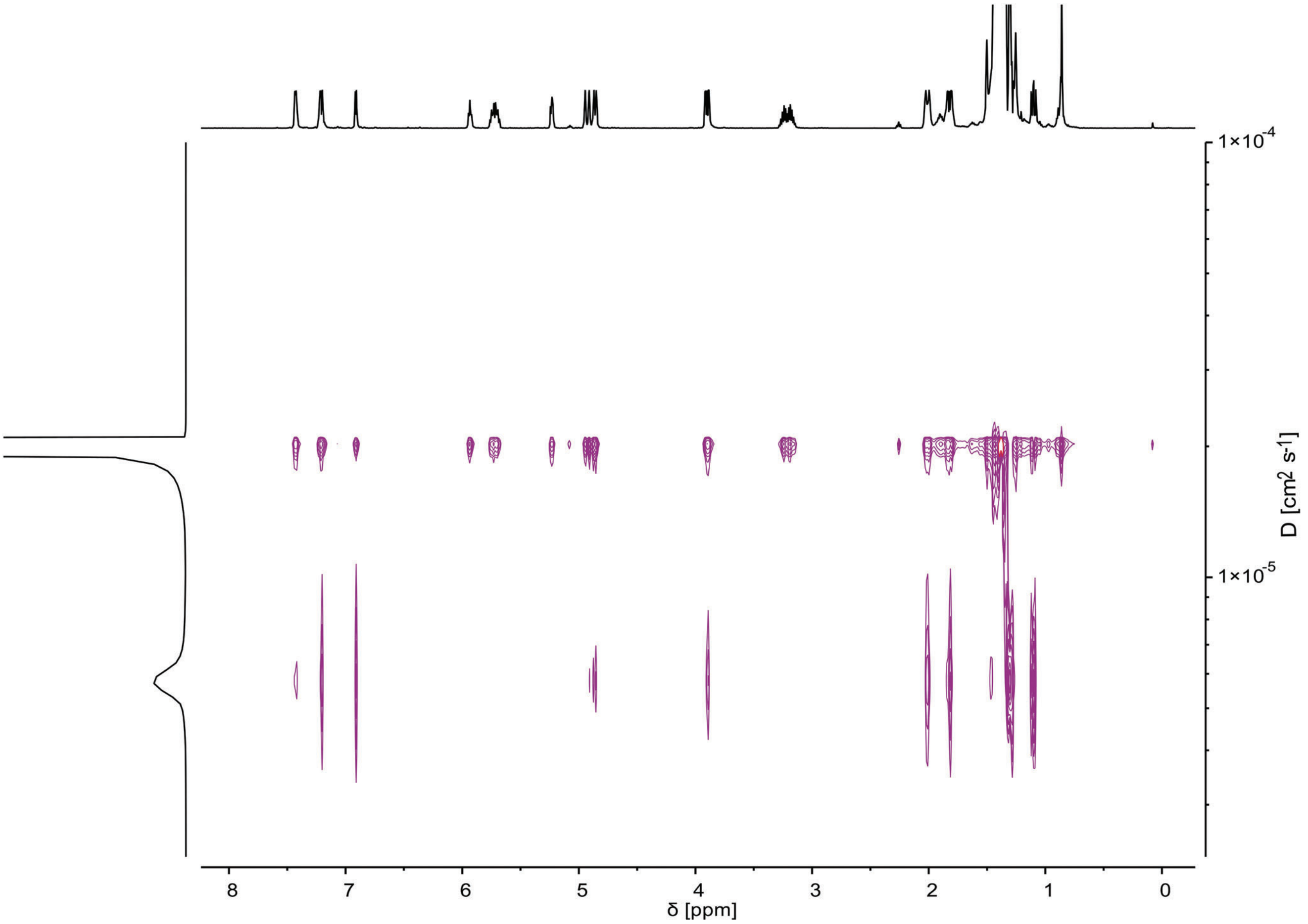

Figure 5. DOSY NMR spectrum of 11 in cyclohexane-d$_{12}$ at a concentration of 1 mм. Two distinct diffusion coefficients can be assigned.

observed for decreasing concentrations. This non-linear increase in fluorescence intensity with increasing dilution may be caused by aggregation of the OPE focal moieties. Fluorescence spectra could only be recorded for **11**, as the macromolecules bearing the OPE dimer and trimer as focal moiety exhibited a fluorescence that was too intense for the detector and thus exceeded the limitations of the available experimental setup. For the same reasons of high absorbance and especially emission, DLS was ruled out for additional experiments regarding the self-assembly of macromolecules **11–13**. Furthermore, other methods like TEM or AFM were not performed, as they were not suitable for the investigation of the dendrons' concentration-dependent self-assembly in cyclohexane solution.

Thus, with these limiting considerations in mind and to confirm the indication of self-assembly provided by the fluorescence spectra, DOSY NMR spectroscopy was performed for solutions of the dendrons in cyclohexane-d_{12}. The DOSY NMR measurements are expected to show two (or more) different diffusion coefficients for the same ^{1}H NMR trace, if a self-assembly takes place. The species with higher diffusion coefficients would be the individual molecule, which is smaller and thus diffuses faster. Consequently, the other species with lower diffusion coefficients would relate to the aggregates, which are larger and thus diffuse slower than the single macromolecules.

The DOSY NMR spectrum for a 1 mм solution of **11** in cyclohexane-d_{12} is shown in **Figure 5**. As expected, two distinct diffusion coefficients were observed. The signals relating to a diffusion coefficient of 2.01×10^{-5} and 5.78×10^{-6} cm^2 s^{-1} can be assigned to the free species of **11** and its aggregates, respectively. DOSY NMR spectra of **12** and **13** showed similar characteristics (see Figures S8 and S9, Supporting Information). For the aggregated species of **11** (Figure 5), signals seem to be missing between 5 and 6 ppm as well as just above 3 ppm. This is a representation artifact, since, for a better overview, the 2D spectrum was not adjusted to the lowest intensity. When all signals are increased in intensity, the missing signals appear, but the 2D spectrum becomes unclear. Thus, it is hereby confirmed that the dendrons show self-assembly properties in cyclohexane, leading to species with reduced diffusion. Diffusion coefficients of the macromolecules and their aggregates in cyclohexane were determined from the DOSY NMR spectra for varying concentrations to investigate the relationship between the diffusion coefficients of the aggregates and the dendron concentration. The obtained values for the diffusion coefficients of the unaggregated macromolecules are listed in **Table 2** and the diffusion coefficients of the aggregates are compared in **Figure 6**.

The unaggregated dendrons all showed similar diffusion coefficients. The small differences in molecular weight could not be

Table 2. Diffusion coefficients of 11, 12, and 13 in a cyclohexane solution of 0.15, 0.3, and 1 mм concentration. Determination of the diffusion coefficients was performed using DOSY NMR spectroscopy.

Concentration [mм]	D(11) [cm^2 s^{-1}]	D(12) [cm^2 s^{-1}]	D(13) [cm^2 s^{-1}]
1.00	2.01×10^{-5}	1.95×10^{-5}	1.96×10^{-5}
0.30	2.01×10^{-5}	2.03×10^{-5}	2.02×10^{-5}
0.15	2.02×10^{-5}	2.03×10^{-5}	1.96×10^{-5}

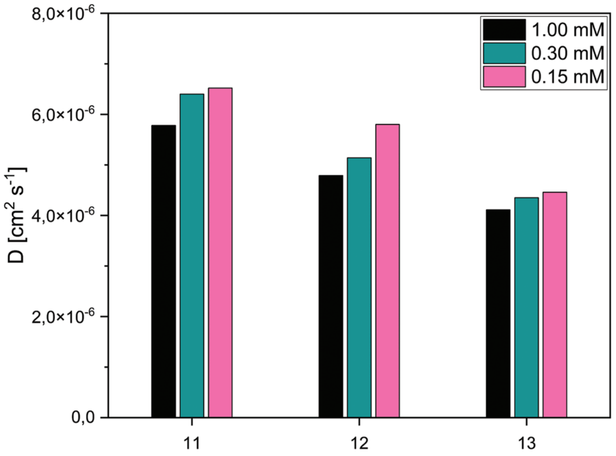

Figure 6. Diffusion coefficients of the aggregates formed by 11, 12, and 13 in cyclohexane solutions of 0.15, 0.3, and 1 mм concentration. Determination of the diffusion coefficients was performed using DOSY NMR spectroscopy.

resolved by DOSY NMR. However, the difference in the diffusion coefficients of the aggregated species is clearly observable. For all three dendrons, the diffusion coefficients of the aggregated species decrease with increasing concentration. Thus, the aggregate size increases with increasing concentration. Furthermore, an increase of the aggregate size with increasing length of the OPE focal moiety can be observed at all investigated concentrations, which can be expected.

In the diffusion trace of the recorded DOSY NMR spectra, the peaks of both species can be integrated separately. By comparing the integral values of the different species for each dendron, the proportions of the unaggregated macromolecules to the aggregates can be determined at varying concentrations. The obtained fraction of the aggregates can then be plotted against the concentration for each dendron (**Figure 7**) to get further insight into the dependency of the aggregation on the concentration and the length of the OPE focal moiety.

With increasing concentration of the dendrons, an increase of the aggregate fraction can be observed for all three OPE lengths. Furthermore, the aggregate fraction at a given concentration is higher for longer OPE focal moieties. This can be explained by the decrease of the focal moieties' solubility in cyclohexane with the increasing length of the OPE and thus an increased driving force for the aggregation.

3. Conclusion

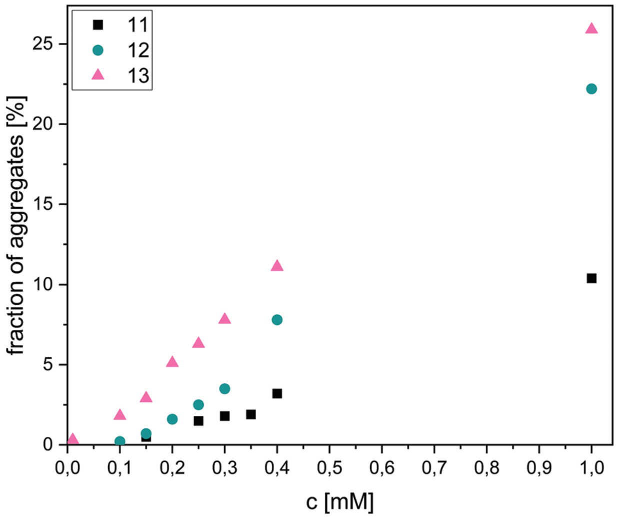

Figure 7. The percentage of macromolecules present as aggregates as determined by integrating the signals on the diffusion trace of the DOSY NMR spectrum.

In this work, the P-3CR was successfully applied for the synthesis of dendrons bearing OPEs as focal moieties in a divergent approach. Furthermore, the self-assembly of the thus obtained uniform macromolecules with varying lengths of the OPE focal moieties in cyclohexane was confirmed and investigated.

For the synthesis of the dendrons, a P-3CR was performed directly on the carboxylic acid group of the OPEs that is installed via the decarboxylative coupling procedure used for their synthesis. The P-3CR with 10-undecenal and 10-isocyanodec-1-ene then directly introduced a branching point to obtain dendrons with good yields. This emphasizes the high efficiency of the P-3CR and its synthetic applicability for the synthesis of dendrons. In total, three different uniform macromolecules were synthesized, varying in the length of the OPE focal moiety.

In all three cases, DOSY NMR spectra showed an aggregated species next to the unaggregated macromolecules. The size of the aggregates was observed to increase with increasing concentrations of the dendrons in all three cases. Moreover, the tendency of the dendrons to form aggregates was investigated by studying the proportions between the unaggregated dendrons and the aggregates at given concentrations. An increase in the OPE length was observed to cause higher fractions of the aggregates at a given concentration compared to shorter OPE focal moieties.

To conclude, the successful synthesis of three different uniform, self-assembling macromolecules with OPEs as focal units highlights the applicability of the P-3CR in the synthesis of dendrons. Furthermore, DOSY NMR spectroscopy was shown to be a suitable and valuable tool for the investigation of the dendrons' self-assembly in the solution that offers advantages to other methods of self-assembly investigations. Apart from these advantages, it should also be mentioned that DOSY NMR spectroscopy does not allow to determine the shape of the aggregates.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

DOSY NMR, oligo(phenylene ethynylene), Passerini three-component reaction, self-assembly, sequence-definition, uniform dendrons

Received: September 16, 2023
Revised: September 30, 2023

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