# Microwave-Assisted Synthesis of 1,5- and 2,6-Linked Naphthylene-Based Ladder Polymers

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ABSTRACT: A series of novel arylene ladder polymers incorporating conjugated 1,5- and 2,6-naphthylene building blocks were synthesized. The polyketone ladder polymer precursors were prepared via a palladium-mediated Suzuki-type cross-coupling reaction using both conventional and microwave heating. While the 2,6-naphthylene polyketone precursor (**2,6-NPK**) was accessible from both heating protocols, the 1,5-naphthylene linked polyketones were only accessible via microwave-assisted ($\mu$W) procedures, and the polymer **1,5-NLP2** is the first example of a ladder polymer consisting exclusively of alternating six-membered rings prepared from this reaction sequence. The solution optical spectra of the final naphthylene ladder polymers exhibit the characteristic spectral shapes with a steep absorption edge and a vibronic fine structure common to fully rigidified ladder structures. The structural modification of the substitution pattern and the linkage positions at the naphthylene unit allows some tuning of the absorption and emission bands of the ladder polymers. The 2,6-naphthylene derivative exhibits an intense blue photoluminescence, while the two 1,5-naphthylene-linked ladder polymers exhibit a red shift of the 0−0 electronic transitions, leading to a blue-green photoluminescence.

## 1. Introduction

Aromatic ladder poly(*p*-phenylene)-type polymers (LPPP)[1] possess a unique set of optoelectronic properties due to their totally planar structure. Consequently, they have attracted widespread attention as components for light-emitting diodes (OLEDs),[2] solid-state laser materials,[3] and two photon pumped fluorescence-based devices.[4] The optoelectronic effects of conjugated polymers are highly dependent on the nature of the building blocks, the pattern in which they are linked, and the type and position of substituents. Naphthalene has a versatile and well-developed substitution chemistry, which provides different patterns for both polymerization and side-chain attachment. Therefore, utilizing the naphthalene unit should allow some tuning of the electronic and optical properties of the resulting semiconducting polymers. However, examples of ladder polymers incorporating higher benzenoid building blocks such as naphthalene in the polymer backbone are rare.[5]

Our proposed synthetic route follows the standard sequence toward arylene ladder polymers.[1] Initially, a polyketone precursor is achieved via a Suzuki-type cross-coupling reaction, followed by two polymer analogue steps. Subsequently the keto group is reacted with methyllithium, and then the resulting tertiary alcohol is cyclized using a Lewis acid. However, despite the present state of knowledge regarding metal-mediated cross-coupling reactions, it still remains difficult to predict the optimum experimental conditions for a particular stratagem. This problem is exacerbated when using conventionally heated cross-coupling reactions to prepare high molecular weight conjugated polymers, as long reaction periods are often required. Furthermore, the molecular weight can have a strong influence on the electronic properties of semiconducting polymers. For example, only high molecular weight poly(3-hexylthiophene) shows sufficient hole mobilities that are required of active material in organic field effect transistors (OFET).[6]

Microwave-assisted heating protocols, on the other hand, allow the energy to be transferred directly to the reactants plus solvents. Recent reports have shown that microwave heating is an efficient tool in enhancing the effectiveness of metal-mediated cross-couplings, thereby allowing the fast screening of a wide range of reaction conditions.[7] Central to the widespread use and acceptance of microwave heating are the advances that have been made to the hardware.[8] The modern commercial microwave equipment offers controllability and reproducibility of synthetic parameters such as temperature, pressure, and reaction times. This offers the possibility for automation and computer-aided control while ensuring a high degree of safety. Herein, we report that the use of microwaves as a heat source is also successful in the preparation of new naphthalene ladder polymers, some of which were not accessible via conventionally heated protocols.

## 2. Results and Discussion

**Synthesis.** The three naphthylene diboronic ester monomers depicted in Figure 1 were the initial target molecules toward the desired naphthylene ladder structures. Bromination of 1,5-dihydroxynaphthalene under acidic conditions[9] gave 2,6-dibromo-1,5-dihydroxynaphthalene (**1**), which was subsequently converted to 2,6-dibromo-1,5-dioctyloxynaphthalene (**2**) by treatment with KOH and octyl bromide in ethanol. 1,5-Dibromo-2,6-dioctyloxynaphthalene (**5**) was prepared in a similar manner. Bromination of 2,6-dihydroxynaphthalene (**4**) under acidic conditions followed by a Williamson reaction gave the ether derivative **5**. In the case of the 1,5-

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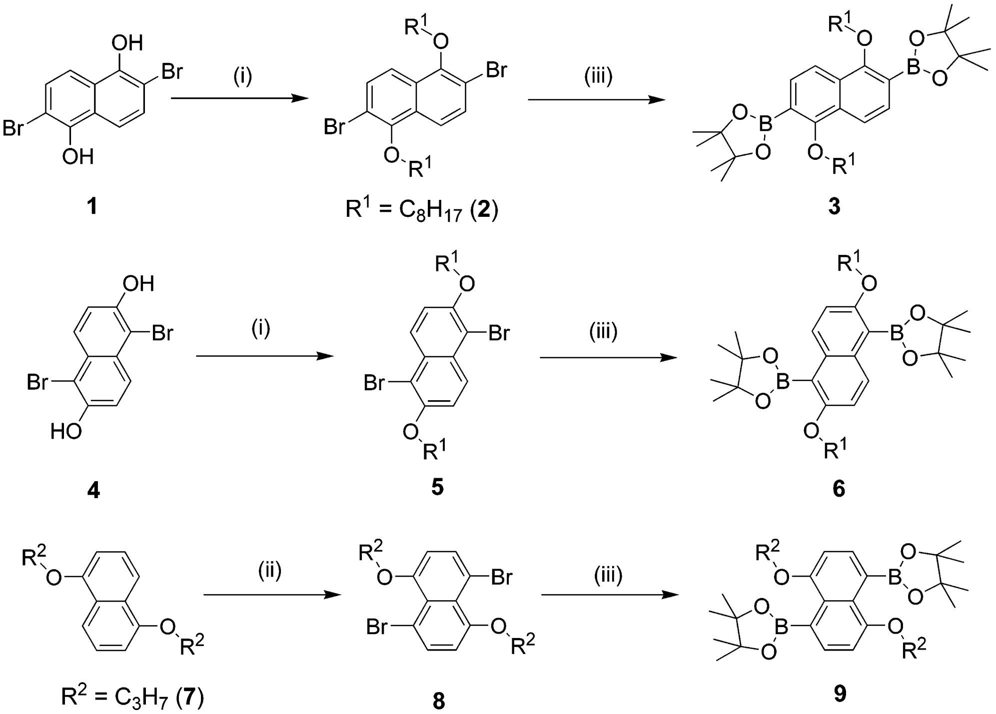

**Figure 1.** Synthetic route to naphthalene boronic ester monomers: (i) KOH, $C_8H_{17}Br$, reflux in ethanol; (ii) NBS in acetonitrile; (iii) BuLi followed by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

dibromo-4,8-dialkoxynaphthalene derivative (**8**) we chose propyloxy side chains to ensure good solubility of the naphthalene diboronic ester monomer and reduce possible steric interactions which may inhibit the formation of the polyketone. To achieve this 1,5-dihydroxynaphthalene was reacted with KOH and propyl bromide in ethanol to give the dipropyloxy derivative **7**, followed by dibromination of **7** to **8** using NBS in acetonitrile.[10] Subsequent reaction of the naphthalene dibromide derivatives **2**, **5**, and **8** with 2.5 equiv of $n$-BuLi at −78 °C and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane gave the corresponding naphthalene diboronic esters in reasonable yields.[11]

The synthetic protocol for the preparation of the naphthylene ladder structures centers on the preparation of the respective precursor polyketones from the relevant naphthalene diboronic esters and the dibromodiketone compound **10** via a Suzuki-type cross-coupling procedure (Figure 2). The first polyketone of our series **2,6-NPK** was prepared from the reaction of **3** and **10** under the standard toluene/2 M aqueous $K_2CO_3$ two-phase Suzuki protocol (Figure 2). However, we found that higher molecular weight polymer was obtained when the more air-stable $Pd(PPh_3)_2Cl_2$ catalyst was used and toluene was replaced by THF. Using conventional heating for 3 days, the polyketone **2,6-NPK** was obtained in 80% yield with a number-average molecular weight of $M_n = 11\,300$ and polydispersity (PD) of 1.8 (as determined by gel permeation chromatography using narrow molecular weight polystyrene as the standard). This corresponds to 12 repeat units (24 arylene units) in the polymer main chain (Table 1). Reducing the reaction time to 1 day gave a lower molecular weight polymer with a higher polydispersity (Table 1). Although it has been reported that 1,5-naphthalenebisboronate undergoes double Suzuki coupling reaction under aqueous conditions, in our hands, neither of the corresponding 1,5-naphthylene linked polyketones were formed via this procedure.[12] **2,6-NPK** was fully characterized by IR, $^1H$ NMR, and $^{13}C$ NMR spectroscopy. The solution IR spectrum displayed a strong absorption band at 1661 $cm^{-1}$ that is assignable to the ketone group.[11] In the $^{13}C$ NMR spectrum the carbon signal of the keto group is found at $\delta = 195.9$ ppm (Figure 3). In addition, there are 12 resonances in the aromatic region and 18 signals associated with the alkyl and alkoxy chains, which is consistent with the proposed structure for **2,6-NPK**.

The next step in the preparation of the naphthylene ladder polymer **2,6-NLP** was the transformation of the keto group to a tertiary alcohol functionality by the reaction of **2,6-NPK** with methyllithium. Prior to this transformation, the polyketone was purified by Soxhlet extraction overnight using ethanol to remove low molecular weight oligomeric components. Full conversion was ensured by checking the IR spectra for the complete disappearance of the carbonyl band at 1661 $cm^{-1}$. Addition of an excess of boron trifluoride etherate to a dichloromethane solution of the polyalcohol was accompanied by the immediate appearance of a strong blue fluorescent reaction solution that is indicative of ring closure. After workup the naphthylene ladder polymer **2,6-NLP** was obtained in 77% yield with $M_n = 18\,400$ and a polydispersity of 1.5. The $^{13}C$ NMR spectrum of **2,6-NLP** revealed the expected 12 signals in the aromatic region, and no other signals were observed which would indicate structural defects or incomplete ring closure. Notably, the ketone resonance at $\delta = 195.9$ ppm is absent, and two signals at $\delta = 54.5$ ppm and $\delta = 27.5$ ppm appear. These correspond to the signals of the quaternary bridging carbon of the methylene bridge and the attached methyl group obtained upon cyclization (Figure 3).

There are many examples of the application of microwave irradiation as a heat source to reduce reaction times and increase the yields of metal-mediated cross-coupling reactions,[7] and so we pursued a microwave-facilitated synthesis of the **1,5-NPK** polyketones. We previously reported that microwave heating is successful

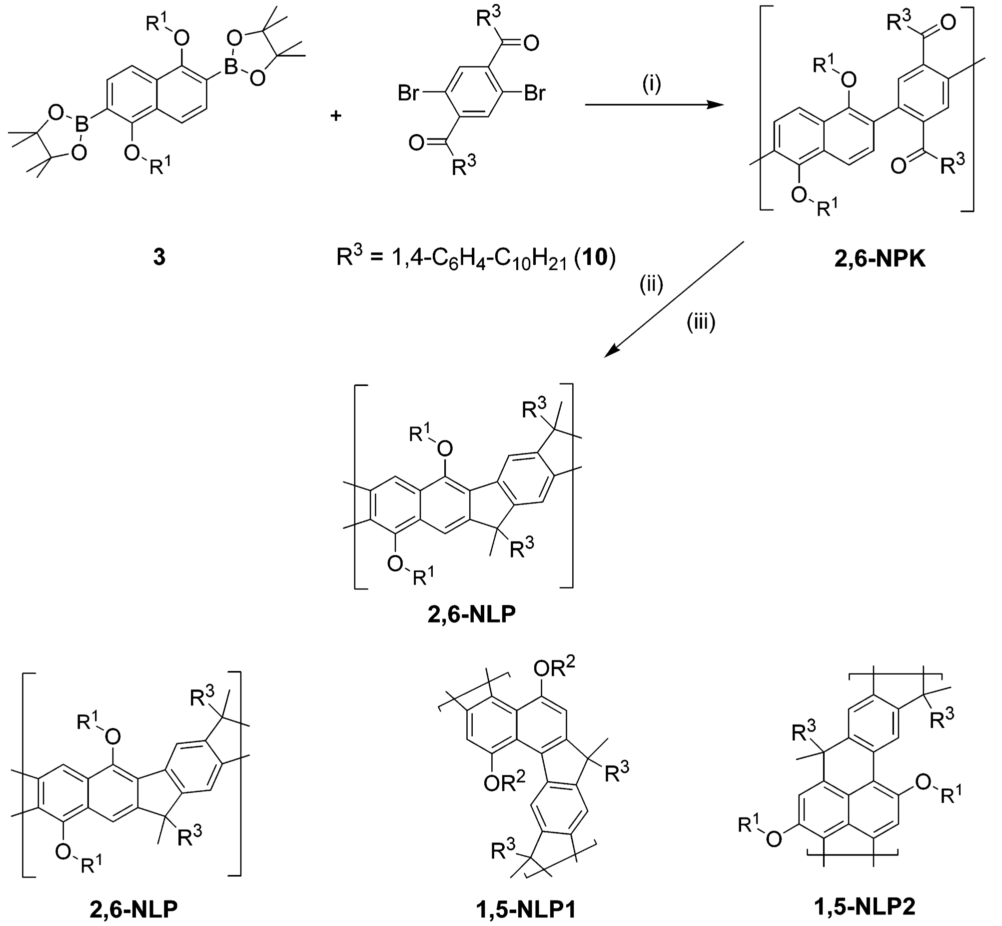

**Figure 2.** Preparative procedure and structure of naphthyl-based ladder polymers: (i) $Pd(PPh_3)_2Cl_2$ in THF/2 M aqueous $K_2CO_3$ using conventional or microwave heating; **1,5-NLP1** and **1,5-NLP2** precursors prepared using KOH in dry THF and microwave heating. (ii) MeLi in THF. (iii) $BF_3{\cdot}OEt_2$ in $CH_2Cl_2$.

**Table 1. Molecular Weight Data and Yields of the Polymers Prepared via Microwave-Assisted and Conventionally Heated Procedures**

| polymer | heating | $M_n$[a] | PD[a] | yield (%) |
|---|---|---|---|---|
| **2,6-NPK** | conventional[b] | 11 300 | 1.7 | 80 |
| **2,6-NPK** | conventional[c] | 3 800 | 2.5 | 83 |
| **2,6-NPK** | μW[d] | 14 200 | 1.8 | 60 |
| **2,6-NPK** | μW[e] | 29 900 | 2.3 | 72 |
| **1,5-NPK1** | μW[e] | 13 600 | 2.4 | 89 |
| **1,5-NPK2** | μW[e] | 9 000 | 1.9 | 78 |
| **2,6-NLP** | | 18 400 | 1.5 | 77 |
| **1,5-NLP1** | | 12 900 | 2.0 | 70 |
| **1,5-NLP2** | | 13 700 | 1.6 | 71 |

[a] Determined by gel permeation chromatography using narrow molecular weight polystyrenes as standards. [b] Aqueous $K_2CO_3$/THF, 3 days. [c] Aqueous $K_2CO_3$/THF, 1 day. [d] Aqueous $K_2CO_3$/THF microwave heating for 12 min (μW 150 W). [e] Solid KOH/THF microwave heating for 10 min (μW 300 W).

**Table 2. Absorption and Emission Data of Naphthylene-Based Ladder Polymers**

| | $\lambda_{max}$ ($CHCl_3$) [nm] | | $\lambda_{max}$ (film) [nm] | |
|---|---|---|---|---|
| polymer | abs | em | abs | em |
| **2,6-NLP** | 420, 448 | 453, 485, 523[a] | 419, 450 | 458, 486, 518[a] |
| **1,5-NLP1** | 451, 480 | 493, 525, 572[b] | 449, 476 | 508, 532[b] |
| **1,5-NLP2** | 439, 466 | 480, 513, 554[a] | 438, 465 | 485, 510, 545[a] |
| **MeLPPP** | 428, 458 | 460, 491, 531[c] | 426, 456 | 464, 494, 530[c] |

[a] $\lambda_{ex}$ = 440 nm. [b] $\lambda_{ex}$ = 460 nm. [c] $\lambda_{ex}$ = 450 nm.

in the preparation of other semiconducting polymers via transition-metal-catalyzed Suzuki and Stille coupling reactions.[13] The application of microwave-assisted heating protocols to essentially nonmiscible solvents such as toluene/water generates “boiling nuclei” and results in an erratic heating pattern (Figure 4). Therefore, the reactions were carried out in sealed 10 mL vials which were filled under glovebox conditions using a THF/water solvent mixture in a single-mode reactor.[14] When the temperature was ramped to ~130 °C over a 2 min period and then held at this temperature with 150 W of power for 9 min, polyketone **2,6-NPK** was obtained with $M_n$ = 14 200 and polydispersity of PD = 1.8 in 61% yield. These results compete well with the best results obtained for **2,6-NPK** when using a conventional heating protocol. Nevertheless, this microwave-assisted technique using a THF/water solvent system was once again not adaptable to the preparation of the isomeric **1,5-NPK** polyketones.

Many novel catalyst–ligand systems have been developed for the synthesis of sterically hindered biaryls.[15] Alternatively, the use of a strong base under nonaqueous conditions is also beneficial for Suzuki coupling reactions involving sterically hindered boronic esters.[16] We tested several nonaqueous combinations of base, solvent, and some of the more common palladium catalysts and found that satisfactory coupling could be best achieved under heterogeneous conditions using powdered KOH as base in dry THF. Applying microwaves (300 W) for 10 min generated a regular reproducible heating pattern (Figure 4), and gave the desired polyketones **1,5-NPK1** and **1,5-NPK2** in good yields with reasonable molecular weights (Table 1). This procedure was reproducible up to concentrations of 0.15

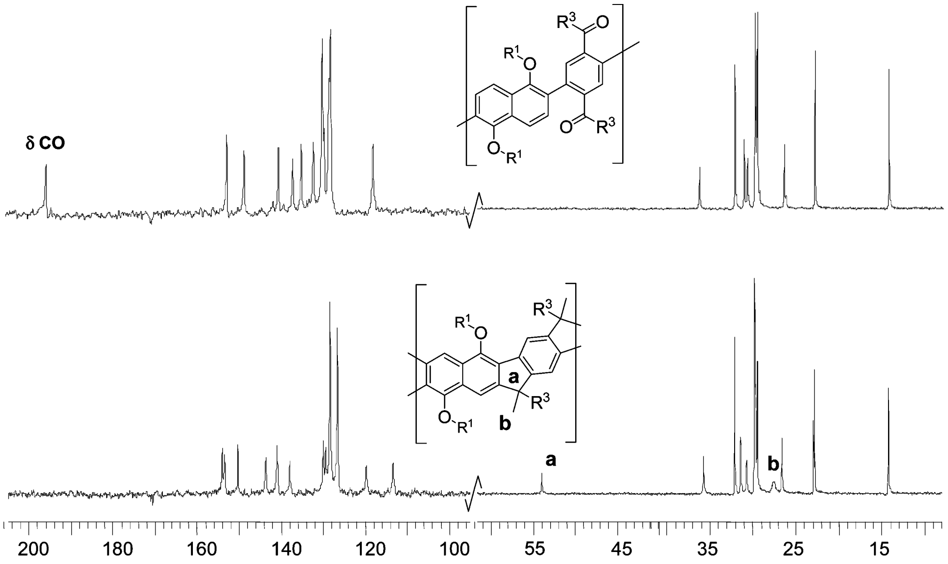

**Figure 3.** $^{13}$C NMR spectrum of **2,6-NPK** (top) and **2,6-NLP** in $C_2D_2Cl_4$.

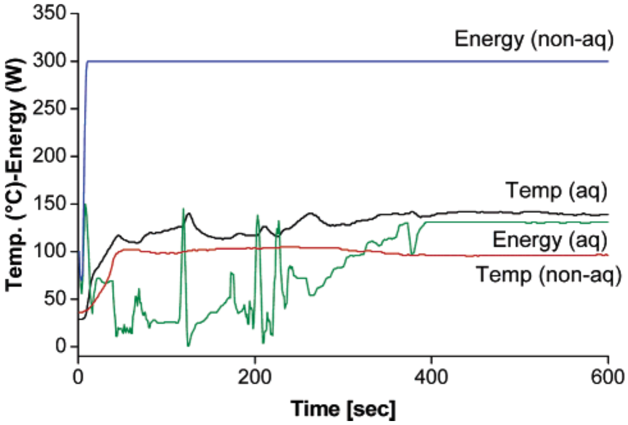

**Figure 4.** Temperature–energy profiles of the microwave-assisted preparation of the polyketones via aqueous (aq) and nonaqueous (non-aq) Suzuki coupling protocols.

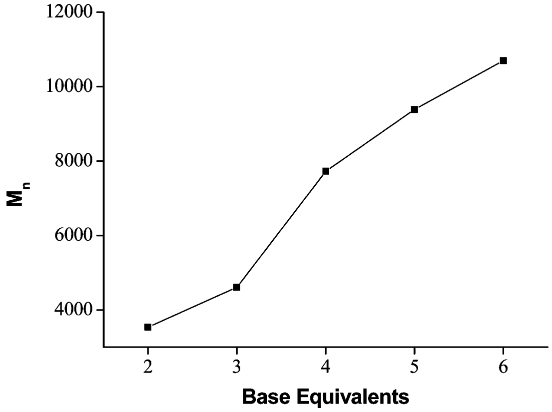

**Figure 5.** Molecular weight of **1,5-NPK1** vs molar quantity of KOH used in nonaqueous microwave-assisted Suzuki protocol.

g of KOH in 2 mL of THF. However, with higher concentrations of base the temperature sometimes spiked due to the KOH sticking to the vessel wall.

Both polyketones were successfully cyclized to their respective ladder polymers: **1,5-NLP1** was obtained with $M_n$ = 12 900 (PD = 2.0) while **1,5-NLP2** had $M_n$ = 13 700 (PD = 1.6). After Soxhlet extraction overnight with acetone the molecular weight of the **1,5-NLP1** sample increased to $M_n$ = 21 400 (PD = 1.5). Using this format, it was also possible to prepare **2,6-NPK** in 72% yield with a distinctly increased number-average molecular weight of $M_n$ = 29 900 (PD = 2.3). After overnight Soxhlet extraction with ethanol this increased to $M_n$ = 38 500 (PD = 1.8). All of the ladder polymers were fully characterized by GPC, UV–vis, photoluminescence, and $^1$H and $^{13}$C NMR spectroscopy. The partial or complete replacement of phenylene units within conjugated polyarylenes with heterocycles or higher benzenoid rings to manipulate their electronic properties is a standard tool. However, examples of 1,5-naphthalene-based polymers are extremely rare and for the most part have been prepared by oxidative or electrochemical polycondensation of the corresponding hydrocarbon monomers.[17] The results presented herein make this nonaqueous microwave-assisted Suzuki-type coupling protocol a viable option toward the preparation of polynaphthylenes.

In general, transmetalation between organopalladium complexes and organoboron compounds does not occur readily without the addition of base because of the low nucleophilicity of the organic group on the boron.[18] The addition of a base such as potassium hydroxide accelerates the transmetalation process by either (i) quarternization of the boron atom, thereby enhancing the nucleophilicity of the organic group, or (ii) via the formation of an hydroxopalladium complex which couple with boronic acids under neutral conditions.[18a,19] In the current microwave-heated synthetic protocols it was found that increasing the quantity of base greatly augmented the molecular weight of the polyketone obtained. For example, when 4 equiv of KOH per boronic ester was used, **1,5-NPK1** was obtained with $M_n$ = 3 500 and PD = 1.9. Increasing the base:boronic ester ratio to 8 and 12 equiv of KOH per diboronic ester led to a doubling and trebling of the molecular weight, respectively (Figure 5).

Generally it is desirable to prepare semiconducting polymers in less polar solvents such as toluene, dichloromethane, or THF so as to ensure high solubility and build up of higher molecular weight material. However, these media have relatively low dielectric constants and loss tangents and therefore are not optimum choices for the absorption and dissipation of the microwave energy to realize effective heating.[20] One of the mechanisms

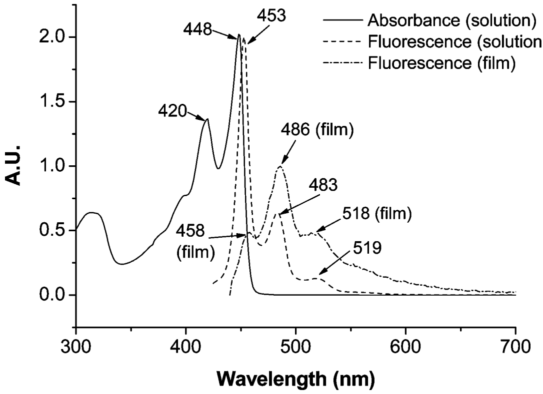

**Figure 6.** Absorption and emission spectra of polymer **2,6-NLP** in chloroform solution and thin film.

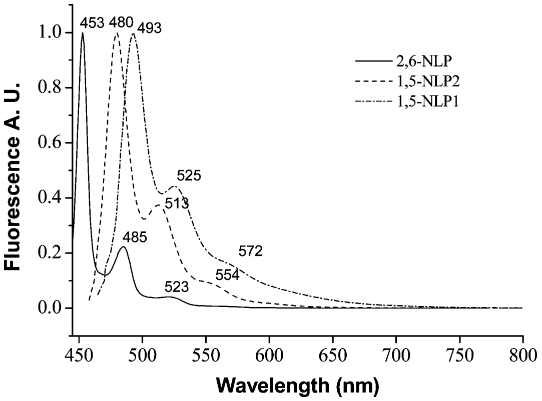

**Figure 7.** Photoluminescence of dilute chloroform solutions of **2,6-NLP**, **1,5-NLP1**, and **1,5-NLP2**.

in which microwaves induce heating is via ionic conduction whereby ionic species attempt to align themselves with the rapidly changing electric field.[8] A number of publications have demonstrated that the addition of a small quantity of an ionic liquid to solvents such as toluene, dichloromethane, or THF greatly improves the efficacy of using microwave irradiation as a heat source.[21] Therefore, we investigated the effects of adding KOH to THF and irradiating the solution with 300 W of power. The effect is not as pronounced as when using ionic liquids, but nonetheless after 2 min the "KOH-spiked" THF sample attained a temperature over 20 degrees higher than the pure THF sample. We propose that the interaction of the base with the microwaves results in the generation of hot spots within the reaction mixture, the concentration of which increases as more KOH is added, and that it is this thermal effect that expedites the cross-coupling reaction.

**Optical Properties.** The optical properties of the three novel naphthylene ladder polymers **2,6-NLP**, **1,5-NLP1**, and **1,5-NLP2** were acquired in both chloroform solutions and as thin films. The well-resolved vibronic structure and the sharp edge of the solution electronic absorption spectra testifies to the rigidity of the ladder polymers and indicates complete cyclization from a flexible open chain to a rigid and more planar structure (Figure 6). **2,6-NLP** exhibits an intense blue photoluminescence (PL) maximum at 453 nm with two well-resolved vibronic sidebands at 483 and 519 nm (Figure 6). The two 1,5-naphthylene ladder polymers are characterized by a somewhat blue-green fluorescence in solution with maxima at 493 nm for **1,5-NLP1** and 480 nm for **1,5-NLP2**. Both **1,5-NLP1** and **1,5-NLP2** display sharp 0−1 sidebands at 525 and 513 nm, respectively (Figure 7), but the 0−2 transitions at ca. 572 and 554 nm are less resolved than for **2,6-NLP**.

The small Stokes shifts between the absorption and photoluminescence maxima reflect the rigid geometry of the ladder polymers.[22] However, the Stokes shifts for both **1,5-NLP1** and **1,5-NLP2** are slightly larger when compared to that of **2,6-NLP**, which may indicate a somewhat reduced intrachain order due to increased distortion within the polymer backbone. **2,6-NLP** is the most stable ladder polymer within this series, displaying no adverse effects to the optical properties upon exposure to sunlight under atmospheric conditions. Solutions of **1,5-NLP1** and **1,5-NLP2** are less stable when exposed to direct sunlight especially in the case when the solutions have not been fully degassed. This behavior of both **1,5-NLP1** and **1,5-NLP2** can be attributed to steric strains within these polymers. It has been previously reported[23] that structurally related hydrocarbons such as perylenes and terylenes that are substituted in the bay positions exhibit considerable deviations from planarity, which resulted in reduced photostability. It is plausible that a similar effect diminishes the photostability of the 1,5-naphthylene linked ladder polymers.

Comparison of the absorption and emission spectra of the three ladder polymers in thin films reveals only small bathochromic shifts in the maxima. The emission spectrum for a thin film of **2,6-NLP** is displayed in Figure 6. The intensity of the 0−0 transition is greatly diminished due to self-absorption in the solid state, but the peak shape and fine structure are clearly apparent with only a minor bathochromic shift to the peak values. Typically, upon formation of aggregates in the solid state a broad featureless emission is observed.[24] A sharp formation in the emission bands, mirror-imaging the absorption bands in the films of all three naphthylene-based ladder polymers, evidences the absence of any strong interchain interaction or aggregate formation.

Often the variations in the optical properties of substituted naphthylene-based oligomers and polymers have been attributed to the mutual distortion of the building blocks due to steric effects.[17,25] Some studies have suggested a sequential hypsochromic shift in the absorption and emission maxima on going from 1,4- to 2,6- and 1,5-linked oligonaphthylenes. However, clear trends have been difficult to establish due to the interplay of geometry and substitution-related effects in these rotationally nonrestricted molecules. The rotation of the neighboring arylene units in the naphthalene ladder polymers presented here is restricted since the polymers are essentially planar. Therefore, the absorption and photoluminescence behavior in these naphthylene-based ladder polymers should be primarily governed by the linking position and the pattern of the alkoxy substitutituents at the naphthylene unit. A blue shift in the $\lambda_{\max,\mathrm{abs}}$ (18−32 nm) and $\lambda_{\max,\mathrm{em}}$ (23−40 nm) values is observed on going from the 1,5-substituted derivatives (**1,5-NLP1**, **1,5-NLP2**) to the 2,6-naphthylene ladder polymer. This would suggest that the 1,5-linkage pattern of the naphthylene units is energetically the most favorable. As expected, within the same 1,5-linkage motif, changing the position of the electron-donating alkoxy substituents from *ortho* (**1,5-NLP2**) to *para* (**1,5-NLP1**) results in a bathochromic shift of $\lambda_{\max,\mathrm{abs}}$ (14 nm) and $\lambda_{\max,\mathrm{em}}$ (13 nm).

With regard to the possible utilization of such ladder polymers as components in future semiconducting polymer-based solid-state laser devices, we fabricated a distributed feedback (DFB) laser device using **2,6-NLP** as the active material. A second-order DFB laser was constructed using a thin layer of 2,6-NLP as the active medium with a grating period of 290 nm and optically excited using a pulsed nitrogen laser (excitation at 1 = 337 nm with 500 ps pulses). For this device structure a sharp laser emission peak at 488.7 nm occurs within the first vibronic sideband of the PL emission with a lasing threshold energy of ca. 480 $\mu$J/cm$^2$ and a spectral half-width of 0.42 nm. A more detailed discussion of the lasing experiments will be published.[26]

## 3. Conclusion

We have developed a microwave-assisted procedure involving a nonaqueous Suzuki-type cross-coupling step for the generation of three novel naphthylene ladder polymers with different linkage and substitution patterns. In the case of **2,6-NPK**, which was prepared via an aqueous coupling protocol using both conventional and microwave-assisted heating, the resulting yields and molecular weights of the ladder polymers obtained are similar. The sterically more hindered 1,5-naphthylene-based polyketones **1,5-NPK1** and **1,5-NPK2** were attainable only by the microwave-heated nonaqueous coupling protocol. The final naphthylene ladder polymers were obtained after polymer analogue cyclization of the polyketone precursors. **1,5-NLP2** is the first example of a ladder polymer consisting exclusively of alternating six-membered rings prepared by this reaction sequence. Through the structural manipulation of the substitution and linkage pattern at the naphthalene unit, it was possible to a certain degree to tune the optical properties of the final ladder polymers. However, for both 1,5-naphthylene-based ladder polymers some steric strain is introduced as evidenced by an increased Stokes shift between absorption and emission and decreased photostability.

## 4. Experimental Section

Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. All reactions were carried out under an argon atmosphere. The solvents were used as commercial p.a. quality. $^1$H and $^{13}$C NMR data were obtained on a Bruker ARX 400 spectrometer. Low-resolution mass spectroscopy was obtained on a Varian MAT 311A operating at 70 eV (electron impact) and reported as *m/z* and percent relative intensity. The UV−vis and fluorescence spectra were recorded on a Jasco V-550 spectrophotometer and a Varian-Cary Eclipse spectrometer, respectively. Gel permeation chromatographic analysis (GPC) utilized PS columns (three columns, 5 $\mu$m gel, pore widths 10$^3$, 10$^5$, and 10$^6$ Å) connected with UV/vis and RI detection. All GPC analyses were performed on solutions of the polymers in THF or toluene at 30 °C with a flow rate of 1 mL/min (concentration of the polymer: ca. 1.5 g/L). The calibration was based on polystyrene standards with narrow molecular weight distribution. Microwave-assisted reactions were performed using a CEM Discover microwave system.

**1,5-Dioctyloxy-2,6-dibromonaphthalene (2).** A solution of 2,6-dibromo-1,5-dihydroxynaphthalene (**1**) (10.0 g, 31.5 mmol) and KOH (5.3 g, 94.5 mmol) in anhydrous ethanol (200 mL) was degassed with argon and heated to reflux. Octyl bromide (16.5 mL, 95.2 mmol) was added slowly, and the solution was refluxed for 12 h. The reaction mixture was cooled and filtered. The solid was then stirred in water (200 mL) for 1 h, filtered, and dried under vacuum. Yield: 77%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.75 (d, *J* = 9.0 Hz, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.95 (m, 4H), 1.59 (m, 4H), 1.37 (m, 16H), 0.92 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ = 152.8, 131.0, 130.1, 119.3, 113.8, 74.6, 31.8, 30.3, 29.5, 29.3, 29.0, 22.7, 14.1. MS (EI, 70 eV): *m/z* = 44 (90.3), 57 (58.34), 316 (45.9), 318 (100.0), 320 (44.7), 540 (6.9), 542 (13.3), 544 (7.2).

**1,5-Dioctyloxynaphthalene-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolate) (3).** *n*-BuLi (4.8 mL of 2.5 M solution, 12.0 mmol) was added dropwise to a solution of **2** (3.0 g, 5.4 mmol) in THF (80 mL) at −78 °C. The solution was stirred at −78 °C for 30 min and then at −10 °C for 10 min. The temperature was again lowered to −78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mL, 19.6 mmol) was added all at once. The solution was allowed to return to room temperature slowly and then stirred overnight before being poured into water. The water was then extracted with dichloromethane, which was subsequently washed with water and brine and dried over MgSO$_4$, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with ethyl acetate/hexanes (1:9) as eluent to give **3** as a yellow solid (52%). $^1$H NMR (400 MHz, CD$_2$Cl$_4$, 25 °C): $\delta$ = 7.82 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 4H), 1.84 (m, 4H), 1.44 (m, 4H), 1.30 (40H), 0.83 (m, 6H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_4$, 25 °C): $\delta$ = 162.5, 131.6, 131.7, 118.4, 117.8, 84.1, 77.3, 32.1, 31.8, 30.7, 29.9, 29.6, 25.2, 23.0, 14.5. MS (EI, 70 eV): *m/z* = 44 (47.7), 55 (49.0), 83 (100.0), 635 (43.9), 636 [M$^+$] (97.9), 637 (39.6). Anal. Calcd for C$_{38}$H$_{62}$B$_2$O$_6$: C, 71.70; H, 9.82. Found: C, 70.88; H, 9.85.

**1,5-Dibromo-2,6-dioctyloxynaphthalene (5).** A solution of 1,5-dibromo-2,6-dihydroxynaphthalene (**4**) (10.0 g, 31.5 mmol) and KOH (5.3 g, 94.5 mmol) in anhydrous ethanol (200 mL) was degassed with argon and heated to reflux. Octyl bromide (16.5 mL, 95.2 mmol) was added slowly, and the solution was refluxed for 12 h. The reaction mixture was cooled and filtered. The solid was then stirred in water (200 mL) for 1 h, filtered, and dried under vacuum. Yield: 83%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.19 (d, *J* = 9.3 Hz, 2H), 7.29 (d, *J* = 9.3 Hz, 2H), 4.15 (t, *J* = 6.6 Hz, 4H), 1.87 (m, 4H), 1.54 (m, 4H), 1.33 (m, 16H), 0.90 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ = 152.4, 129.3, 127.2, 116.8, 109.5, 70.4, 31.8, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1. MS (EI, 70 eV): *m/z* = 316 (58.97), 318 (100.0), 320 (58.1), 540 (12.4), 542 [M$^+$] (22.3), 544 (12.8).

**2,6-Dioctyloxynaphthalene-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolate) (6).** *n*-Buli (4.8 mL, 12.0 mmol) was added dropwise to a solution of **5** (3.0 g, 5.4 mmol) in THF (80 mL) at −78 °C. The solution was stirred at −78 °C for 30 min and then at −10 °C for 10 min. The temperature was again lowered to −78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mL, 19.6 mmol) was added all at once. The solution was allowed to return to room temperature slowly and then stirred overnight before being poured into water. The water was then extracted with dichloromethane, which was subsequently washed with water and brine and dried over MgSO$_4$, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with ethyl acetate/hexanes (1:9) as eluent to give 2.5 g (67%). $^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 25 °C): $\delta$ = 7.83 (d, *J* = 9.1 Hz, 2H), 7.13 (d, *J* = 9.1 Hz, 2H), 4.0 (t, 4H), 1.71 (m, 4H), 1.41 (s, 28H), 1.28 (16H), 0.91 (t, 6H). $^{13}$C NMR (100 MHz, C$_2$D$_2$Cl$_4$, 25 °C): $\delta$ = 159.5, 132.6, 130.5, 115.3, 114.8, 84.1, 70.0, 32.1, 30.0, 29.8, 29.6, 26.5, 25.3, 23.0, 14.5. MS (EI, 70 eV): *m/z* = 44 (54.1), 55 (55.9), 57 (59.0), 83 (100.0), 635 (66.3), 636 [M$^+$] (100.0), 637 (63.3). Anal. Calcd for C$_{38}$H$_{62}$B$_2$O$_6$: C, 71.70; H, 9.82. Found: C, 69.61; H, 9.76.

**1,5-Dipropyloxynaphthalene (7).** A solution of 1,5-naphthalenediol (10.0 g, 62.4 mmol) and KOH (10.5 g, 187 mmol) in anhydrous ethanol (200 mL) was degassed with argon and heated to reflux. Propyl bromide (17.0 mL, 187 mmol) was added slowly, and the solution was refluxed for 12 h. The reaction mixture was cooled and filtered. The solid was then stirred in water (200 mL) for 1 h, filtered, and dried under vacuum. Yield: 88%. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.20 (d, *J* = 8.3 Hz, 2H), 6.73 (dd, 2H), 6.23 (d, *J* = 7.7 Hz, 2H), 43.48 (t, 4H), 1.33 (m, 4H), 0.53 (t, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ = 153.0, 125.2, 123.8, 112.5, 104.0, 68.1, 21.1, 9.4. MS (EI, 70 eV): *m/z* = 160 (100.0), 244 [M$^+$] (43.7).

**1,5-Dipropyloxy-4,8-dibromonaphthalene (8).** *N*-Bromsuccinimide (4.8 g, 27.0 mmol) in acetonitrile (20 mL) was added dropwise to a suspension of **7** (3.0 g, 12.3 mmol) in acetonitrile (40 mL), which was cooled in an ice bath. The ice bath was removed, and the resulting solution was stirred at room temperature overnight. The solid was collected by filtration, washed with acetonitrile (50 mL), and then with methanol (100 mL) to give **8** in 63% yield. $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 7.68$ (d, $J = 8.6$ Hz, 2H), 6.68 (d, $J = 7.7$ Hz, 2H), 4.0 (t, 4H), 1.98 (m, 4H), 1.15 (t, 6H). $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 154.6$, 133.6, 126.2, 108.5, 106.9, 71.4, 22.4, 11.0. MS (EI, 70 eV): $m/z = 44$ (63.4), 238 (53.8), 316 (52.6), 318 (100.0), 320 (48.7), 400 (38.2), 402 [M$^+$] (79.9), 404 (37.1).

**1,5-Dipropyloxynaphthalene-4,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolate) (9).** *n*-Buli (6.6 mL of 2.5 M solution, 16.5 mmol) was added dropwise to a solution of **8** (3.0 g, 7.5 mmol) in THF (80 mL) at −78 °C. The solution was stirred at −78 °C for 30 min and then at −10 °C for 30 min. The temperature was again lowered to −78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mL, 19.6 mmol) was added all at once. The solution was allowed to return to room temperature slowly and then stirred overnight before being poured into water. The water was then extracted with dichloromethane, which was subsequently washed with water and brine and dried over $\mathrm{MgSO_4}$, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with ethyl acetate/hexanes (1:9) as eluent to give a yellow powder (59%). $^1$H NMR (400 MHz, $\mathrm{C_2D_2Cl_2}$, 25 °C): $\delta = 7.33$ (d, $J = 7.6$ Hz, 2H), 6.68 (d, $J = 7.6$ Hz, 2H), 4.22 (t, 4H), 1.78 (m, 4H), 1.35 (s, 24H), 0.91 (t, 6H). $^{13}$C NMR (100 MHz, $\mathrm{C_2D_2Cl_2}$, 25 °C): $\delta = 155.2$, 130.7, 129.4, 118.7, 106.0, 83.4, 25.4, 70.1, 21.7, 10.7. MS (EI, 70 eV): $m/z = 44$ (44.8), 55 (40.9), 83 (100.0), 495 (25.4), 496 [M$^+$] (60.0), 497 (16.0). Anal. Calcd for $\mathrm{C_{28}H_{42}B_2O_6}$: C, 67.77; H, 8.53. Found: C, 67.75; H, 8.37.

**Synthesis of 2,6-NPK.** A dried 100 mL flask was charged with 4,4′-didecyl-2′,5′-dibromoterephthalophenone (**10**) (0.3 g, 0.47 mmol), **3** (0.34 g, 0.47 mmol), and $\mathrm{PdCl_2(PPh_3)_2}$ (0.015 mg, 0.021 mmol) and dissolved in degassed THF (20 mL). $\mathrm{K_2CO_3}$ (0.6 g, 4.34 mmol in 5 mL of degassed water) was added, and the reaction mixture was refluxed for 3 days. The polymer was extracted into chloroform, and the organic phase was washed with water and dried over $\mathrm{MgSO_4}$, and the solvent was removed by rotary evaporation. The residue was taken up in chloroform and precipitated into MeOH/2 M HCl (10:1) to give **2,6-NPK** in 80% yield with molecular weight data $M_\mathrm{n} = 11\,300$ and PD = 1.7. After extracting the crude solid with ethanol and reprecipitation, the polyketone was obtained in 72% yield. $M_\mathrm{n} = 13\,700$, PD = 1.3. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 7.75$ (2H), 7.69 (6H), 7.25 (2H), 7.11 (4H), 3.76 (4H), 2.55 (4H), 1.57 (8H), 1.24 (48H), 0.85 (12H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 195.9$ (CO), 153.0, 148.9, 140.7, 137.3, 135.3, 132.5, 130.4, 129.9, 128.8, 128.7, 128.4, 118.4, 74.7, 36.2, 32.1, 31.9, 31.0, 30.6, 30.5, 29.8, 29.7, 29.6, 29.4, 29.2, 26.3, 26.1, 22.8, 22.7, 14.2. IR ($\mathrm{CHCl_3}$): $\nu$(CO) = 1661 cm$^{-1}$.

**Synthesis of 2,6-NPK via Microwave Synthesis.** A stock solution of an equimolar quantity of the monomers **3** and **10** in degassed THF was prepared. $\mathrm{PdCl_2(PPh_3)_2}$ (~4%) was added to a 10 mL vial in a glovebox and sealed under argon. To this was added the monomer stock solution and 10 mol equiv from a degassed 4 M $\mathrm{K_2CO_3}$ solution and then irradiated with microwaves (150 W) for 12 min. A maximum temperature of ~110 °C was maintained by applying air cooling so that in general the power remained constant during the reaction. The polyketone was obtained after the standard workup mentioned above. For the nonaqueous procedure, the vial was charged with all the reagents and sealed under argon. THF was then added, and the solution was irradiated with microwaves (300 W) for 10 min. The residue was dissolved in chloroform precipitated into MeOH/2 M HCl (10:1). Yield: 60%. $M_\mathrm{n} = 14\,200$, PD = 1.8.

**Synthesis of 2,6-NLP.** An excess of MeLi (1.6 M solution) was added to a solution of **2,6-NPK** in toluene (40 mL) and stirred for 10 min. THF (20 mL) was added, and the mixture was stirred for 16 h at room temperature. Chloroform was added, and the solution was extracted with 2 M HCl. The organic phase was dried with $\mathrm{Na_2SO_4}$, and the solvent was removed under reduced pressure. The polyalcohol was dissolved in dichloromethane (30 mL) and treated with an excess of boron trifluoride. The solution was stirred for 2 h, and then an EtOH/water mixture (70 mL 2:5) was added and the organic layer was extracted several times with water. The organic phase was dried with $\mathrm{Na_2SO_4}$, and the solvent was removed by rotary evaporation. The residue was dissolved in chloroform and precipitated into methanol to give **2,6-NLP** in 70% yield with $M_\mathrm{n} = 18\,400$ and PD = 1.5. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 8.00$ (2H), 7.76 (2H), 7.21 (4H), 7.01 (4H), 3.76 (4H), 2.55 (4H), 1.8−2.1 (7H), 1.2−1.6 (52H), 0.8−1.0 (12H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 154.0$, 153.4, 150.3, 143.7, 141.0, 138.0, 130.0, 129.4, 128.4, 126.6, 119.8, 113.4, 74.3, 54.5, 35.7, 32.1, 31.4, 30.7, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 27.5, 26.6, 26.5, 22.9, 22.8, 14.3, 14.2.

**Synthesis of 1,5-NPK1 via Nonaqueous Microwave Procedure.** All the reagents were added to a 10 mL vial and sealed under argon. Dry THF (2 mL) was added, and the reaction was irradiated with microwaves (300 W) for 10 min with air-cooling to keep the temperature between 110 and 115 °C. The polyketone was obtained after the standard workup mentioned above. The residue was taken up in chloroform and precipitated into methanol which gave polyketone in 89% yield with $M_\mathrm{n} = 13\,600$ and PD = 2.4. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 7.7$−6.7 (14H), 3.8 (4H), 2.5 (4H), 1.3 (36H), 0.9 (12H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 200.5$ (CO), 158.4, 150.3, 145.4, 142.4, 138.9, 132.5, 132.1, 131.4, 130.8, 130.4, 128.8, 109.1, 70.5, 36.2, 36.0, 32.0, 31.0, 29.7, 29.5, 29.4, 25.4, 22.8, 22.5, 14.2, 11.0. IR ($\mathrm{CHCl_3}$): $\nu$(CO) = 1649 cm$^{-1}$.

**Synthesis of 1,5-NLP1.** Following the procedure described for the cyclization of **2,6-NPK**. After the workup as described for **2,6-NLP,** the residue was taken up in chloroform and precipitated into methanol to give **1,5-NLP1** in 70% yield with $M_\mathrm{n} = 12\,900$ and PD = 2.0. After extracting the crude solid with ethanol for 2 days and reprecipitation the ladder polymer was obtained in 38% yield. $M_\mathrm{n} = 21\,400$, PD = 1.5. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 8.00$ (2H), 7.18 (4H), 7.00 (4H), 6.72 (2H), 3.87 (4H), 2.51 (6H), 1.90 (4H), 1.55 (4H), 1.25 (32H), 0.86 (6H), 0.57 (6H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 156.1$, 154.5, 153.2, 142.9, 140.5, 128.3, 126.9, 124.3, 121.8, 105.3, 71.4, 54.3, 35.7, 32.1, 31.4, 31.3, 29.9, 29.8, 29.7, 29.5, 25.5, 22.8, 21.7, 14.2, 10.5.

**Synthesis of 1,5-NPK2 via Nonaqueous Microwave Procedure.** Following the procedure described for the nonaqueous synthesis of **1,5-NPK1**. The polyketone was obtained after the standard workup mentioned above. The residue was taken up in chloroform and precipitated into methanol which gave the polymer in 78% yield with $M_\mathrm{n} = 9000$ and PD = 1.9. After extracting the crude solid with ethanol for 1 day and reprecipitation the polyketone was obtained in 61% yield. $M_\mathrm{n} = 13\,000$, PD = 1.6. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 7.7$−6.7 (14H), 3.9 (4H), 2.5 (4H), 0.4−1.8 (68H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): 151.5, 151.1, 148.5, 141.9, 135.4, 133.4, 130.1, 129.2, 128.0, 126.7, 122.7, 114.9, 69.7, 36.3, 32.3, 32.2, 31.4, 30.0, 29.9, 29.8, 29.7, 26.2, 26.1, 23.0, 14.5. IR ($\mathrm{CHCl_3}$): $\nu$(CO) = 1663 cm$^{-1}$.

**Synthesis of 1,5-NLP2.** Following the procedure described for the cyclization of **2,6-NPK**. After the workup as described for **2,6-NLP** the residue was taken up in chloroform and precipitated into methanol to give 1,5-NLP1 in 71% yield with $M_\mathrm{n} = 13\,700$ and PD = 1.6. $^1$H NMR (400 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 8.5$ (2H), 6.5−7.7 (10H), 3.7 (4H), 2.5 (4H), 0.4−2.0 (74H). $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_4}$, 80 °C): $\delta = 153.2$, 148.5, 142.0, 140.3, 134.9, 129.2, 129.1, 128.9, 127.9, 125.1, 118.6, 70.4, 49.4, 35.8, 34.5, 32.1, 31.5, 31.4, 29.8, 29.6, 29.5, 29.4, 29.3, 28.7, 26.2, 26.1, 22.8, 14.2.

**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra of **3** in $\mathrm{C_2D_2Cl_4}$, $^1$H and $^{13}$C NMR spectra of **6** in $\mathrm{C_2D_2Cl_4}$, NMR spectrum of **9** in $\mathrm{C_2D_2Cl_4}$, $^{13}$C NMR spectrum of **9** in $\mathrm{C_2D_2Cl_4}$, and IR spectra of **2,6-NPK**, **1,5-NPK1**, and

**1,5-NPK2** in chloroform. This material is available free of charge via the Internet at http://pubs.acs.org.

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