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Synthesis of a Novel Poly(iptycene) Ladder Polymer

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ABSTRACT: A self-polymerizable AB-type monomer for Diels−Alder (D−A) polymerization was prepared, and its polymerization was carried out in the melt phase and at high pressure in solution. The former method generated only low-molecular-weight polymer, but the latter one offered an efficient polymerization with increased molecular weight, due to the effect of high pressure on reactions with a negative activation volume. A pyridinium *p*-toluenesulfonate-catalyzed dehydration reaction of the D−A polymer led to a novel aromatic ladder polymer, poly(iptycene), which is soluble in common organic solvents and stable up to 350 °C. The NMR and UV−vis spectra of these polymers match the spectra of their corresponding model compounds, the synthesis of which is also reported.

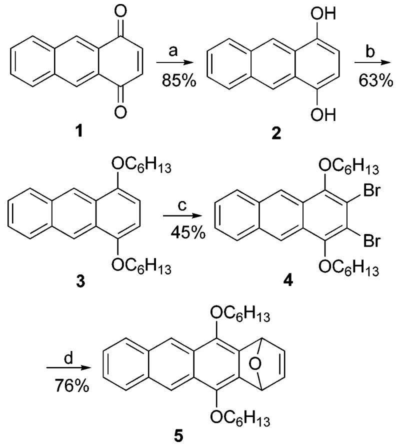
Introduction

The term "iptycene" was coined by Hart as the base terminology to describe a family of molecules containing a number of arene units joined together to form the bridges of [2.2.2] bicyclic ring systems.[1] The prefixes (e.g., tri- and penti-) indicate the number of interconnected arene planes. Since the first synthesis of triptycene by Bartlett in 1942,[2] a variety of iptycene molecules have been synthesized and investigated.[1,3−6] The rigid framework of iptycenes has been useful for the study of intramolecular charge transfer,[7] atropisomerism,[8] and molecular gears.[9] Recently, iptycenes and iptycene-containing polymers were found to be able to direct molecular organizations in liquid crystal and polymer matrices, using the minimization of the free volume between the arene rings of iptycene frameworks as an organizational driving force.[6c,10] The insertion of fused iptycene units into a polymer backbone was also found to improve solubility,[11,12] enhance mechanical properties,[13] and lower the dielectric constants[14] of the polymer. More interestingly, the incorporation of iptycene units into conjugated polymers improves their solid-state luminescence quantum yields, stability, and thereby their exciton transport properties.[11,15] The latter is the result of the three-dimensional shape persistence of iptycene units, which helps to isolate the polymer backbones from each other to avoid self-quenching often observed in condensed phases.

Although iptycenes and iptycene-containing polymers have been extensively investigated, the reports of polymers composed solely of iptycene scaffolds, which are referred to as poly(iptycene)s, are rare.[11,16−18] Poly(iptycene), which contains both the rigid iptycene unit and a double-stranded ladder polymer structure, is expected to exhibit a two-dimensional disk with a shape-persistent structure and high degrees of internal free volume.[11,19] The free volume of these structures has been demonstrated to display unique organization in stretched polymer films.[18]

Iptycenes are typically prepared by Diels−Alder (D−A) reactions between anthracene or higher acenes (as the diene) and various dienophiles, such as quinones, arynes (dehydrobenzenes), and benzofused endoxides. The quinone route generally requires multistep syntheses,[2,3a,5c] and the aryne reactions require harsh conditions and results in low yields.[1,3a,3b] In contrast, the reactions between anthracene derivatives and benzofused endoxides represent an efficient method for preparing triptycene precursors that can be readily dehydrated.[1] Our lab has previously demonstrated that a closely related ladder polymer could be prepared from a triptycene-containing AB-type monomer, which bears both anthracene and endoxide groups.[18] Since AB-type monomers contain both the diene and dienophile, they possess the perfect stoichiometry for a D−A polymerization. In the present paper, we report the synthesis of a new AB-type monomer, 1,4-epoxy-5,12-dihexyloxy-1,4-dihydrotetracene (**5**) (Scheme 1), and its polymerization at neat melt and under high pressure in solution. A novel poly(iptycene) ladder polymer was successfully prepared from the dehydration of the above D−A polyaddition polymer.

Scheme 1. Synthesis of Monomer 5[a]



[a] Reagents and conditions: (a) $Na_2S_2O_4$, *p*-dioxane, H_2O, rt; (b) $C_6H_{13}Br$, K_2CO_3, 18-crown-6, DMF, 60 °C; (c) NBS, DMF, rt; (d) furan, THF, PhLi, 0 °C.

Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic route to **5**, an AB-type monomer containing both the anthracene and endoxide functionality, as diene and dienophile, respectively. The 1,4-anthraquinone (**1**), which was prepared from quinizarin according to a literature procedure,[20] was converted into 1,4-dihexyloxyanthracene (**3**) by reduction with sodium dithionate and subsequent alkylation. The hexyloxy side chain was introduced to improve the polymer solubility because aromatic

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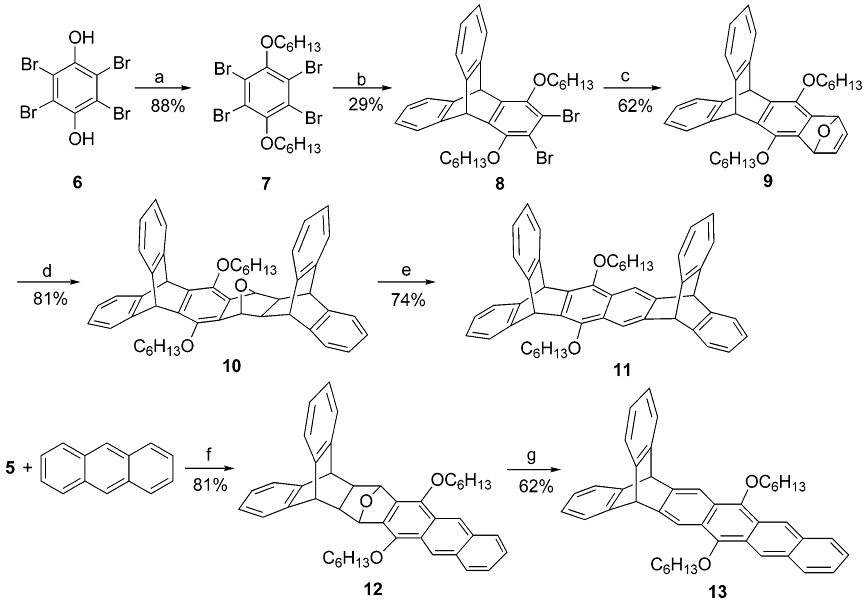
Scheme 2. Syntheses of Model Compounds[a]



[a] Reagents and conditions: (a) K_2CO_3, $C_6H_{13}Br$, 18-crown-6, DMF, 70 °C; (b) anthracene, toluene, *n*-BuLi, 0 °C; (c) furan, toluene, *n*-BuLi, −30 °C; (d) anthracene, xylene, 140 °C; (e) pyridinium *p*-toluenesulfonate, acetic anhydride, 120 °C; (f) xylene, 140 °C; (g) pyridinium *p*-toluenesulfonate, acetic anhydride, 120 °C.

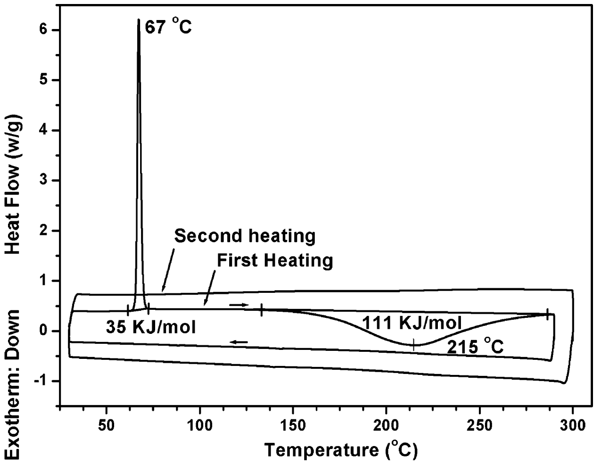


Figure 1. DSC trace of monomer **5** showing melt endotherm and thermolysis exotherm.

ladder polymers generally have poor solubility in organic solvents.[19] The brominated intermediate (**4**) was prepared by stirring a mixture of **3** and *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) at room temperature.[18] In the presence of excess furan, treatment of **4** with phenyllithium (PhLi) in anhydrous tetrahydrofuran (THF) afforded **5** as slightly yellow needlelike crystals. The yield over four steps is 18%.

Syntheses of Model Compounds. For spectroscopic references, we synthesized model compounds **10** and **11** (Scheme 2), which resemble the repeating unit of the initial D−A polyaddition polymer and the expected poly(iptycene) after dehydration, respectively. The synthetic strategy was adapted from a procedure previously reported by Hart.[1] Compound **8** was prepared by the D−A reaction of anthracene and an aryne generated in situ from **7**. Compound **9** was prepared from **8** by a procedure similar to that used for the synthesis of **5**. The final step to model compound **10** involved a D−A reaction between anthracene and endoxide (**9**), which gave a single adduct **10** in 81% yield. In the ^{1}H NMR spectrum of **10** (Figure 2), three singlets at 2.22, 4.36, and 5.01 ppm are assigned to the methine proton and the two sets of adjacent aliphatic bridgehead protons. These features are consistent with the NMR results of previously reported similar molecules,[4g,h,j] which were proposed to form a rigid framework with dihedral angles close to 90° between adjacent sets of nonequivalent bridgehead protons, resulting in almost no coupling. Single-crystal X-ray structural analysis confirmed that molecules bearing such NMR spectral features are the exo-adduct of the D−A reaction between anthracene and endoxide.[21] The dehydration of **10** produced model compound **11** as a white solid. Model compound **13**, which resembles the terminal tetracene group of expected poly(iptycene) chain, was prepared in two steps. A D−A reaction between **5** and anthracene afforded the single adduct **12**, which demonstrated similar ^{1}H NMR spectral features as **10** and could be attributed as the exo-adduct. Finally, the dehydration of **12** afforded model compound **13** as a yellow solid.

Thermal Analysis by Differential Scanning Calorimetry (DSC). DSC was used to investigate the onset and breadth of various thermally induced transitions and reactions. Figure 1 displays the DSC trace of compound **5**, showing the D−A polymerization. On heating **5**, a sharp endotherm peak was seen at 67 °C, which corresponds to the melting point of **5**. Further heating generated a large broad exotherm peak with onset temperature at 162 °C and maximum at 215 °C, which could be attributed to an 111 kJ/mol exothermicity from the D−A reaction of **5**. The large breadth of the exotherm peak indicates the slow rate of the D−A reaction. After heating to 290 °C and cooling to 30 °C, no subsequent crystallization was observed. Furthermore, heating of the sample to back 300 °C did not reveal any endothermic melting or exothermic transitions, indicating that the monomer was entirely consumed in the first heating cycle. Analysis of the DSC sample by gel permeation chromatography (GPC) confirmed that polymerization had occurred, yielding a mixture of oligomers with the number-average molecular weight (M_n) = 2800 Da and polydispersity index (PDI) = 2.8.

Preparation of Polymer P1. Following the DSC result, we carried out a polymerization of **5** in the neat melt by heating the solid at 170 °C (Scheme 3). Unfortunately, only low-molecular-weight polymers with M_n = 5400−6000 Da were

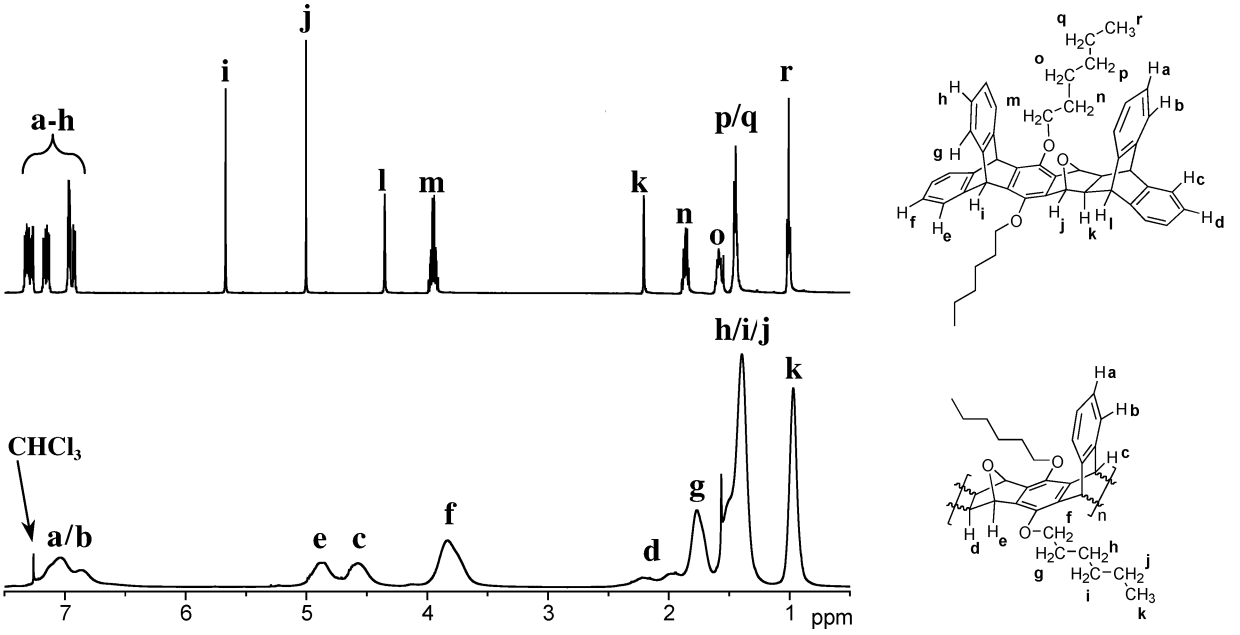


Figure 2. ^{1}H NMR (solvent: CDCl$_3$) spectra of model compound **10** (top) and polymer **P1** (M_n = 16 400 Da, PDI = 3.6) (bottom).

Scheme 3. Polymer Synthesis

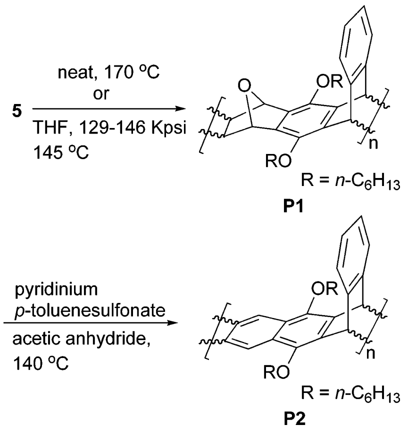


Table 1. Summary of Hyperbaric Polymerization Data

					P1		P2	
entry	[M]^a (M)	temp (°C)	time (h)	pressure (psi)	M_n^b (Da)	PDI	M_n^b (Da)	PDI
1	0.50	145	5	128 900	6 100	2.2	n/a	n/a
2	0.88	145	5	139 600	9 400	2.7	10 900	2.4
3	1.01	145	5	145 800	11 100	3.3	12 600	2.6
4	1.50	145	5	145 800	16 400	3.6	16 300	2.5

[a] Monomer concentration. [b] Molecular weights determined by GPC in THF against polystyrene standards.

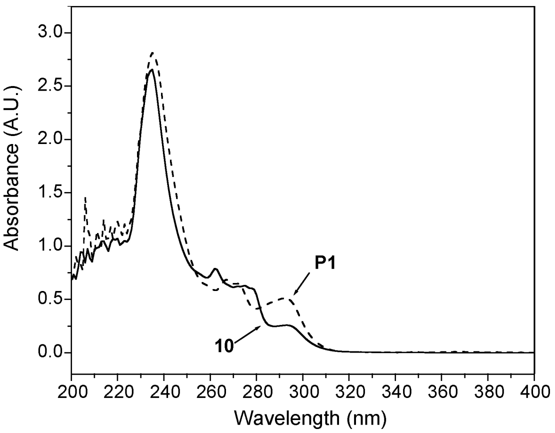


Figure 3. UV–vis absorption spectra of model compound **10** and polymer **P1** (M_n = 16 400 Da, PDI = 3.6) measured in methylene chloride.

obtained. Since iptycene molecules generally have high melting points, the low molecular weight can be attributed to the high melting point of the formed oligomers. Additionally, attempts to polymerize **5** in *o*-dichlorobenzene at 180 °C under atmospheric pressure only afforded a mixture of oligomers.

It is well-known that the application of pressure accelerates some reactions whose transition states present a net contraction in volume.[22]

$$\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_T$$

The D–A reaction is strongly pressure accelerated because it has a large negative activation volumes $\Delta V^{\ddagger}$ (−25 to −45 cm^3 mol^{-1}).[22d,e] Hence, the polymerization of **5** under high pressure in the solution phase was investigated,[18] and the results are summarized in Table 1. Four monomer solutions of different concentrations in THF were heated at 145 °C under the pressures of 129–146 kpsi for 5 h (Scheme 3). As expected, increased pressure yielded polymers (**P1**, Scheme 3) with a higher degree of polymerization, and the higher monomer concentrations led to polymers with higher molecular weight, which is typical for condensation polymerizations. However, the molecular weight could not be further improved by increasing the monomer concentration because the final reaction mixture from 1.5 M monomer solution was found to be viscous gel-like material. **P1** was obtained as a white solid and is soluble in methylene chloride, chloroform, and THF. Both the ^{1}H and ^{13}C NMR spectra of **P1** were identical to those of the polymer obtained from the melt. Figure 2 displays the ^{1}H NMR spectra of **P1** and the peak assignments, together with the spectrum of model compound **10**. The spectral features of **P1** are in accord with those of **10**. The broad and unstructured signals of **P1** reflect the ribbon structure produced by D–A polymerization with a complex sequence of stereoisomers.[22] Specifically, the asymmetrical broad peak observed at 6.7–7.3 ppm suggests that the D–A polymerization proceeds with the formation of stereoisomers. As indicated earlier, model compound **10** was obtained as a single adduct, and the endoxide reacts exclusively on the

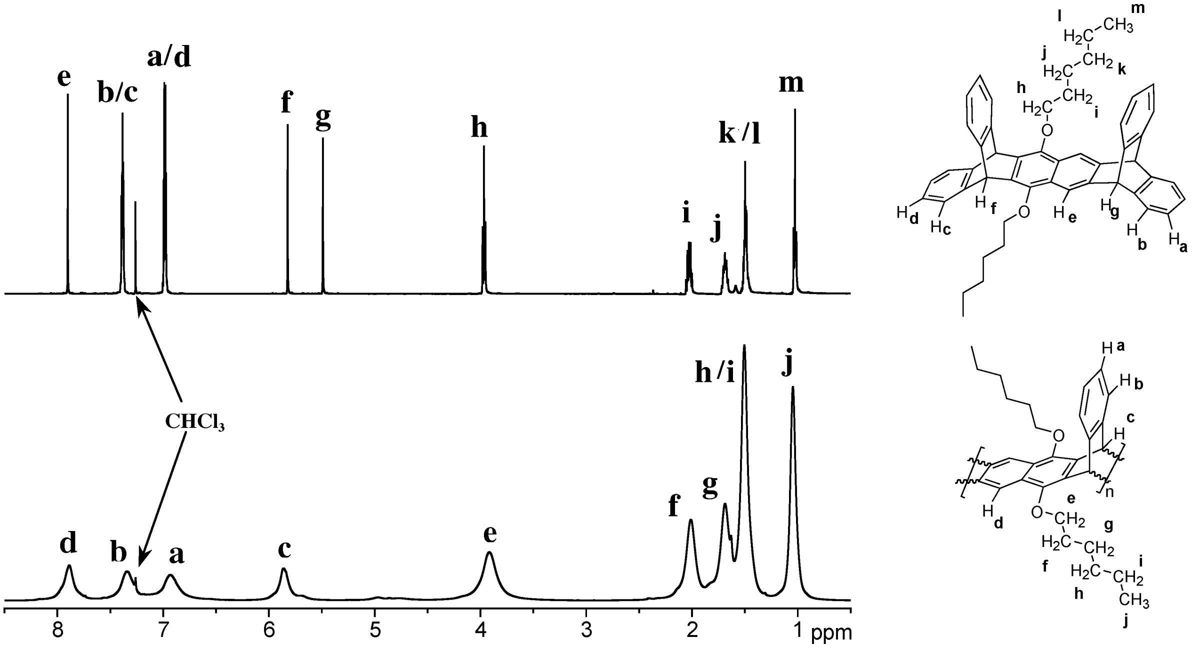


Figure 4. ^{1}H NMR (solvent: $CDCl_3$) spectra of model compound **11** (top) and polymer **P2** (M_n = 16 300 Da, PDI = 2.5) (bottom).

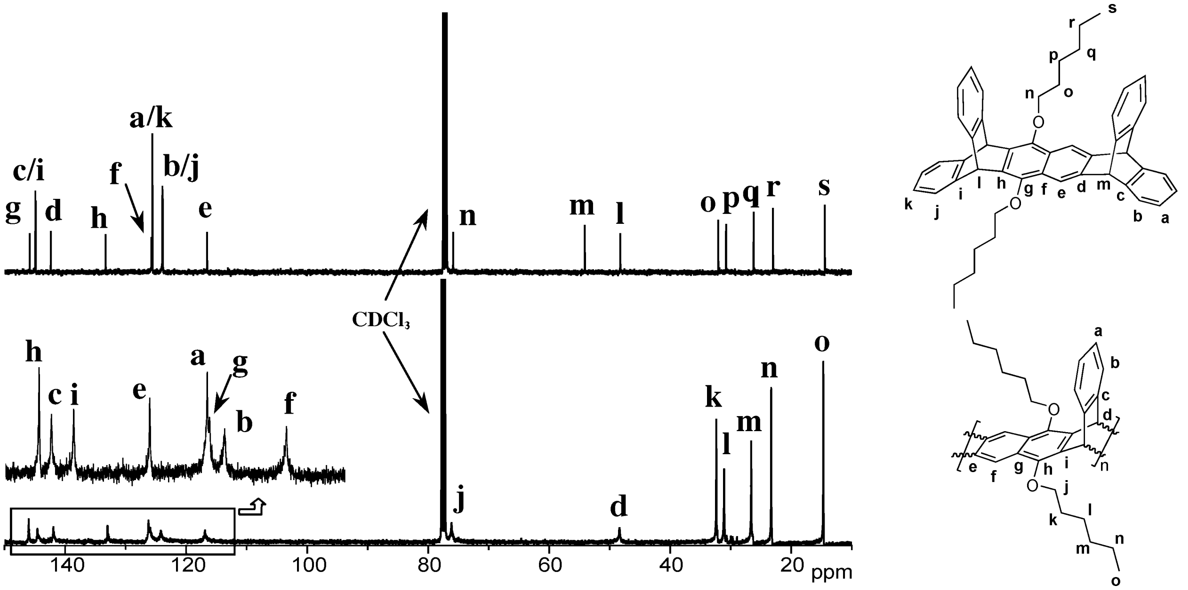


Figure 5. ^{13}C NMR (solvent: $CDCl_3$) spectra of model compound **11** (top) and polymer **P2** (M_n = 16 300 Da, PDI = 2.5) (bottom).

exo surface. The stereochemical disorder in the polymer is therefore likely due to reaction at the inequivalent faces of the anthracene in **5**. This is also consistent with the two broad peaks at 1.8−2.5 ppm, which can be assigned to the methine protons (H_d of **P1**, Figure 2) in different isomeric configurations. Only one singlet was observed for the corresponding methine proton of **10**. A complicated ^{13}C spectrum of **P1**, which demonstrates more aromatic carbon atoms than those of one repeating unit, provides further support for isomeric structures in **P1**. However, the stereochemical possibilities in **P1** are numerous and cannot be conclusively determined. Although we only observe exo D−A adducts in the synthesis of **10** and **12**, the high-pressure conditions and other macromolecular structural constraints could lead to some endo D−A product.[23] There are further different orientations of the dienophile (endoxide group) with respect to each face of each diene (anthracene group) for a total of four potential stereoisomers for endo D−A linkage as well as four possible stereoisomers for exo D−A linkage. Upon conversion to **P2**, both the endo and exo linkage give the same stereoisomers, and hence as shown in Figure 4, the NMR spectrum of **P2** is less complex. Interestingly, the UV−vis absorption spectrum of **P1** is almost identical to that of the model compound **10** (Figure 3).

Preparation of Polymer P2. We have found that the dehydration of a D−A polymer similar to **P1** was unsuccessful by either catalytic *p*-toluenesulfonic acid in toluene or direct thermolysis, and incomplete dehydration and decomposition of the polymer were observed. With careful optimization, the dehydration of **P1** was realized by employing pyridinium *p*-toluenesulfonate and acetic anhydride (Scheme 3). **P2** was obtained as light yellow solid with no significant change of molecular weight compared to its precursor polymer **P1** (Table 1). It is readily soluble in organic solvents including methylene chloride, chloroform, and THF due to both the side-chain and three-dimensional iptycene units. Thermogravimetric analysis (TGA) of **P2** revealed thermal stability up to 350 °C under a helium atmosphere.

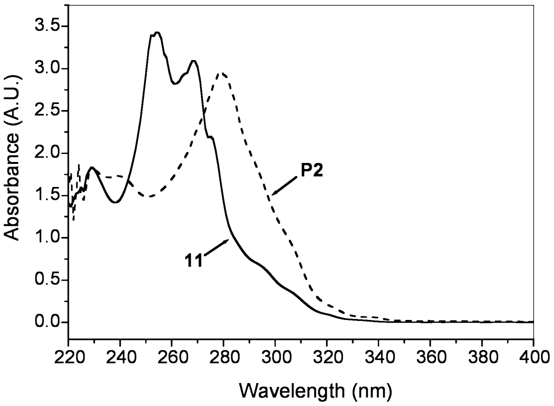


Figure 6. UV−vis absorption spectra of model compound **11** and polymer **P2** (M_n = 16 300 Da, PDI = 2.5) measured in methylene chloride.

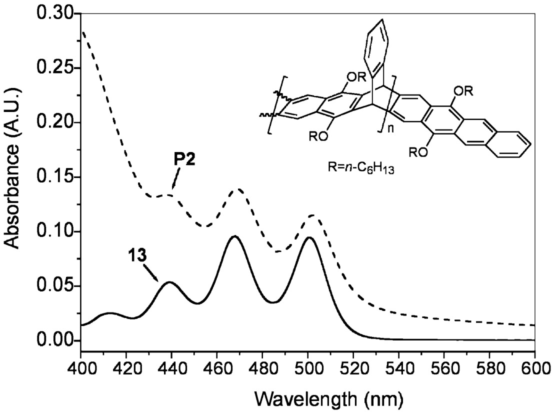


Figure 7. UV−vis absorption spectra of model compound **13** and low-molecular-weight polymer **P2** (M_n = 6000 Da, PDI = 2.3), with inset showing the proposed structure of polymer with one end group.

Successful dehydration of **P1** to **P2** was confirmed by comparison of the ^{1}H and ^{13}C NMR spectra of **P2** and model compound **11** (Figures 4 and 5). Compared to **P1**, the ^{1}H spectrum of **P2** is well resolved, partly due to the elimination of stereochemistry by dehydration. The peak at 7.90 ppm in the ^{1}H spectrum of **P2** is attributed to the proton on naphthalene unit, and the other two aromatic peaks at 7.36 and 6.95 ppm are assigned to the two aromatic protons on the benzene ring. The signal of bridgehead proton is observed at 5.88 ppm, which is typical for iptycene molecules. The signal at 5.49 ppm in the spectrum of **11** does not have a counterpart in the polymer spectrum because it is from the other bridgehead proton (H_g) of **11** (Figure 4). Accordingly, the signal at 54.1 ppm in the ^{13}C spectrum of **11**, which is attributed to the above-mentioned bridgehead carbon atom (C_m), also has no counterpart in the ^{13}C spectrum of **P2** (Figure 5). Other peaks observed at 3.93, 2.02, 1.70, 1.52, and 1.06 ppm in the ^{1}H spectrum of **P2** are assigned to the protons of hexyloxy side chain. More informative results came from the ^{13}C spectrum of **P2**, which has an excellent match with that of model compound **11** (Figure 5). The **P2** spectrum shows signals of eight aromatic carbons and seven saturated carbons, consistent with the structure of repeating unit of the expected poly(iptycene). On the basis of the ^{13}C peak assignments of model compound **11**, which are made by using the combined techniques of distortionless enhancement by polarization transfer (DEPT) and heteronuclear multiple-bond correlation (HMBC), we can make the complete ^{13}C peak assignments of **P2** as illustrated in Figure 5.

Figure 6 shows the UV−vis absorption spectra of model compounds **11** and **P2** in methylene chloride. The spectrum of **P2** shows a considerable bathochromic shift of the absorption λ_{max} as compared with compound **11**, which may result from the extended hyperconjugation between the arene rings of iptycene units.[24] Interestingly, the UV−vis absorption spectrum of a sample of the low-molecular-weight **P2** (M_n = 6000 Da, PDI = 2.3), shown in Figure 7 together with the spectrum of model compound **13**, clearly demonstrates the features of a tetracene unit, which is believed to be the end group of the polymer chain. This feature may be useful for studying the alignment of these polymers in liquid crystals and polymeric matrices.

Conclusion

A bifunctional AB-type monomer (**5**) capable of undergoing D−A polymerization was synthesized, and its thermally induced polymerization was investigated by DSC. Polymerization of **5** in the melt phase yielded only low-molecular-weight D−A polymer. However, running the polymerization under increased pressure in solution yielded polymers (**P1**) with a higher degree of polymerization. Additionally, a novel poly(iptycene) ladder polymer (**P2**) was successfully produced from the dehydration of the precursor polymer (**P1**), employing pyridinium *p*-toluenesulfonate and acetic anhydride. The structures of both **P1** and **P2** were assigned by correlating their NMR spectra with model compounds. The secondary structure of the poly(iptycene) and its alignment in liquid crystals are currently under study.

Experimental Section

Materials. NBS was recrystallized from water. Anthracene was recrystallized from hexane. Furan was distilled from K_2CO_3 prior use. The 1,4-anthraquinone (**1**) was prepared according to literature procedures.[20] All other chemicals of reagent grade were obtained from Aldrich Chemical Co. or Alfa Aesar and used without further purification.

General Method and Instrumentation. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. High-pressure reactions were carried out on a custom-built isostatic compaction system from Harwood Engineering Co., Inc. (Walpole, MA).[18] Column chromatography was performed using silica gel (40−63 μm) from SiliCycle. NMR spectra were obtained on Varian Mercury 300 MHz, Bruker Advance 400 MHz, or Varian Inova 500 MHz instruments. The ^{1}H and ^{13}C chemical shifts are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0 and referenced to residual solvent. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices Inc.) and were not corrected. Polymer molecular weights were determined on a HP series 1100 GPC system in THF (1 mg/mL sample concentration) at room temperature vs polystyrene standards. Transition temperatures were determined by DSC using a TA Instruments Q1000 DSC at scan rates of 10 °C/min. TGA was carried out with TA Instruments Q50 under helium at a scan rate of 20 °C/min. UV−vis spectra were obtained from Hewlett-Packard 8452A diode array UV−vis spectrophotometer.

Synthesis of Monomer. 1,4-Dihydroxyanthracene (2). A solution of $Na_2S_2O_4$ (30 g) in *p*-dioxane (170 mL) and nitrogen-bubbled water (170 mL) was added to 1,4-anthraquinone (8.6 g, 41.3 mmol) under Ar. After the mixture was stirred at 25 °C for 3.5 h, an extra $Na_2S_2O_4$ (16 g) was added in one portion. The mixture was stirred for an additional 4 h and then poured into 400 mL of water. The precipitate was collected by filtration, washed with water, and dried in a vacuum, leading to a greenish-yellow solid as crude product (7.4 g, 85%), which was used without further purification; mp 170−172 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 9.57 (s, 2H), 8.66 (s, 2H), 8.08 (dd, J = 6.3, 3,3 Hz, 2H), 7.46 (dd, J = 6.6, 3.3 Hz, 2H), 6.62 (s, 2H). ^{13}C NMR (75 MHz, DMSO-

d_6): 145.4, 130.5, 128.5, 125.4, 125.2, 120.7, 105.6. HRMS calcd for $C_{14}H_{10}O_2$ (M^+): 210.0675; found: 210.0665.

1,4-Dihexyloxyanthracene (3). In an oven-dried 250 mL round-bottom flask equipped with a stir bar were combined **2** (4.0 g, 19.0 mmol), 1-bromohexane (9.4 mL, 67.0 mmol), potassium carbonate (21 g, 152.2 mmol), 18-crown-6 (0.1 g), and nitrogen-bubbled DMF (150 mL). The mixture was stirred under Ar at 60 °C for 5 d. After cooling to room temperature, the mixture was poured into 300 mL of water and the product was extracted with CH_2Cl_2. The organic layer was washed by dilute NH_4Cl aqueous solution and saturated NaCl aqueous solution and then dried over $MgSO_4$. Evaporation of the solvent yielded a brown solid which was recrystallized from methanol to yield yellow needlelike crystals (4.5 g, 63%); mp 69−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.80 (s, 2H), 8.06 (dd, $J = 6.3, 3.3$ Hz, 2H), 7.48 (dd, $J = 6.3, 3.3$ Hz, 2H), 6.60 (s, 2H), 4.16 (t, $J = 6.5$ Hz, 4H), 2.00 (m, 4H), 1.63 (m, 4H), 1.44 (m, 8H), 0.96 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 149.2, 131.8, 129.0, 126.2, 125.8, 121.2, 102.3, 68.8, 32.1, 29.8, 26.5, 23.1, 14.6. HRMS calcd for $C_{26}H_{34}O_2$ (M^+): 378.2553; found: 378.2556.

2,3-Dibromo-1,4-dihexyloxyanthracene (4). A mixture of **3** (4.4 g, 11.6 mmol), NBS (4.5 g, 25.3 mmol), and nitrogen-bubbled DMF (90 mL) was stirred under Ar at room temperature for 5 h. The mixture was poured into 450 mL of dilute NH_4Cl aqueous solution, and the product was extracted by CH_2Cl_2. The extracts were combined and washed by 0.1 N aqueous solution of NaOH, water, and saturated NaCl aqueous solution in sequence and then dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane:CH_2Cl_2 (4:1, v/v) afforded 2.8 g (45%) of product as light yellow solid; mp 56−57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.65 (s, 2H), 8.05 (dd, $J = 6.3, 3.3$ Hz, 2H), 7.54 (dd, $J = 6.6, 3.3$ Hz, 2H), 4.17 (t, $J = 6.6$ Hz, 4H), 2.05 (m, 4H), 1.68 (m, 4H), 1.46 (m, 8H), 0.97 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 150.7, 132.5, 129.0, 127.1, 126.9, 122.4, 115.3, 74.8, 32.2, 30.7, 26.2, 23.1, 14.6. HRMS calcd for $C_{26}H_{32}Br_2O_2$ (M^+): 534.0764; found: 534.0785.

1,4-Epoxy-5,12-dihexyloxy-1,4-dihydrotetracene (5). Under Ar, a stirred mixture of **4** (2.8 g, 5.2 mmol), furan (30 mL), and anhydrous THF (80 mL) was cooled by an ice−water bath. A solution of PhLi (4.5 mL, 1.5−1.7 M) was then added dropwise over the course of 5 h. After the addition of PhLi, the mixture was stirred at 0 °C for an additional 2 h and then allowed to warm to room temperature slowly and stirred overnight. Methanol (2 mL) was added slowly to quench the reaction. The reaction mixture was poured into water, and the product was extracted by CH_2Cl_2. The organic layer was washed by saturated NaCl aqueous solution and dried over $MgSO_4$. Solvent was removed in vacuo. Purification by column chromatography on silica gel with CH_2Cl_2:hexane (2:1, v/v) and recrystallization from hexane afforded the product as slightly yellow needlelike crystals (1.76 g, 76%); mp 62−63 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.58 (s, 2H), 8.00 (dd, $J = 6.3, 3.3$ Hz, 2H), 7.47 (dd, $J = 6.5, 3.3$ Hz, 2H), 6.95 (s, 2H), 6.13 (s, 2H), 4.22 (m, 4H), 1.96 (m, 4H), 1.62 (m, 4H), 1.44 (m, 8H), 0.96 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 143.0, 140.0, 132.0, 128.6, 127.6, 125.9, 125.7, 121.6, 80.5, 74.2, 31.9, 30.5, 26.1, 22.9, 14.3. HRMS calcd for $C_{30}H_{36}O_3$ (M^+): 444.2659; found: 444.2658.

Syntheses of Model Compounds. 1,2,4,5-Tetrabromo-3,6-dihexyloxybenzene (7). In an oven-dried 500 mL round-bottom flask equipped with a stir bar were combined 1,2,4,5-tetrabromohydroquinone (**6**) (10.9 g, 25.6 mmol), 1-bromohexane (15 mL, 107 mmol), potassium carbonate (38 g, 275 mmol), 18-crown-6 (0.1 g), and nitrogen-bubbled DMF (290 mL). The mixture was stirred under Ar at 70 °C for 5 d. The workup procedure is similar to that of the preparation of **3**. Recrystallization from CH_2CH_2/methanol yielded colorless crystals (13.3 g, 88%); mp 50−51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 3.98 (t, $J = 6.6$ Hz, 4H), 1.88 (m, 4H), 1.51 (m, 4H), 1.38 (m, 8H), 0.93 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 152.1, 121.6, 73.8, 31.9, 30.1, 25.7, 22.8, 14.3. HRMS calcd for $C_{18}H_{26}Br_4O_2$ (M^+): 589.8661; found: 589.8677.

2,3-Dibromo-1,4-dihexyloxytriptycene (8). To a stirred solution of **7** (3.0 g, 5.0 mmol) and anthracene (2.1 g, 12 mmol) in anhydrous toluene (180 mL) under Ar at 0 °C was added dropwise a solution of *n*-butyllithium (*n*-BuLi) (3.5 mL, 1.6 M, 5.6 mmol) over the course of 3.5 h. After the addition of *n*-BuLi, the reaction mixture was allowed to warm to room temperature slowly and stirred overnight. The mixture was quenched by water and extracted with diethyl ether. The organic layer was washed with water and saturated NaCl aqueous solution and dried over $MgSO_4$. The solvent was evaporated, and the residue was recrystallized in acetone. The colorless crystals (unreacted anthracene) were removed by filtration. The filtrate was concentrated, and the residue was chromatographed on silica gel with hexane, affording product as colorless crystals (0.9 g, 29%); mp 73−75 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.40 (dd, $J = 5.3, 3.3$ Hz, 4H), 7.04 (dd, $J = 5.5, 3.0$ Hz, 4H), 5.75 (s, 2H), 3.94 (t, $J = 6.8$ Hz, 4H), 1.98 (m, 4H), 1.64 (m, 4H), 1.46 (m, 8H), 0.99 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 149.0, 144.6, 139.8, 125.8, 124.1, 118.0, 75.3, 49.0, 32.0, 30.4, 26.1, 22.9, 14.4. HRMS calcd for $C_{32}H_{36}Br_2O_2$ (M^+): 610.1077; found: 610.1071.

6,11(1′,2′)-Benzeno-1,4-epoxy-5,12-dihexyloxy-1,4,6,11-tetrahydrotetracene (9). To a stirred solution of **8** (0.69 g, 1.1 mmol) and furan (8 mL) in anhydrous toluene (80 mL) under Ar at −30 °C was added dropwise a solution of *n*-BuLi (0.8 mL, 1.6 M, 1.3 mmol) over the course of 3 h. After the addition of *n*-BuLi, the mixture was stirred at −30 °C for an additional 2 h and then allowed to warm to room temperature slowly and stirred overnight. The reaction mixture was quenched by water and diluted with 150 mL of diethyl ether. The product was washed with water and saturated NaCl aqueous solution and dried over $MgSO_4$. The solvent was evaporated, and the residue was chromatographed on silica gel with CH_2Cl_2:hexane (1:1, v/v, slowly up to 2:1), affording product as a colorless, highly viscous liquid (0.36 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.36 (dd, $J = 5.1, 3.3$ Hz, 4H), 6.98 (m, 6H), 5.82 (pt, 2H), 5.71 (s, 2H), 3.94 (m, 4H), 1.84 (m, 4H), 1.57 (m, 4H), 1.43 (m, 8H), 0.97 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.0, 145.8, 144.6, 142.9, 137.8, 136.5, 125.2, 123.8, 81.0, 74.9, 48.4, 31.9, 30.4, 26.1, 22.9, 14.3. HRMS calcd for $C_{36}H_{40}O_3$ (M^+): 520.2972; found: 520.2964.

***exo*-5,16(1′,2′):8,13(1″,2″)-Dibenzeno-6,15-epoxy-7,14-dihexyloxy-5,5a,6,8,13,15,15a,16-octahydrohexacene (10).** A solution of **9** (0.36 g, 0.7 mmol) and anthracene (0.20 g, 1.1 mmol) in xylene (15 mL) was refluxed for 3 days. The reaction mixture was concentrated, and the residue was chromatographed on silica gel with CH_2Cl_2:hexane (1:1, v/v), affording the product as a colorless solid (0.40 g, 81%); mp 108−110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.33 (dd, $J = 5.2, 3.2$ Hz, 2H), 7.31 (dd, $J = 5.2, 3.2$ Hz, 2H), 7.28 (dd, $J = 5.2, 3.2$ Hz, 2H), 7.18 (dd, $J = 5.2, 3.2$ Hz, 2H), 7.15 (dd, $J = 5.2, 3.2$ Hz, 2H), 6.98 (m, 4H), 6.93 (dd, $J = 5.2, 3.2$ Hz, 2H), 5.68 (s, 2H), 5.01 (s, 2H), 4.36 (s, 2H), 3.95 (m, 4H), 2.22 (s, 2H), 1.87 (m, 4H), 1.60 (m, 4H), 1.46 (m, 8H), 1.02 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.7, 145.6, 144.2, 142.7, 141.6, 138.2, 135.9, 126.2, 125.9, 125.2, 125.17, 124.0, 123.8, 123.76, 123.68, 80.0, 74.7, 49.2, 48.4, 47.6, 31.9, 30.4, 26.1, 23.0, 14.4. HRMS calcd for $C_{50}H_{50}O_3$ (M^+): 698.3754; found: 698.3740.

5,16(1′,2′):8,13(1″,2″)-Dibenzeno-7,14-dihexyloxy-5,8,13,16-tetrahydrohexacene (11). A mixture of **10** (76 mg, 0.11 mmol), pyridinium *p*-toluenesulfonate (270 mg, 1.1 mmol), and acetic anhydride (4 mL) was stirred under Ar at 120 °C for 15 h. The mixture was then allowed to cool to room temperature. The white precipitate was collected by filtration, washed thoroughly with methanol, and dried in a vacuum (55 mg, 74%); mp 256−258 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.90 (s, 2H), 7.39 (m, 8H), 6.99 (m, 8H), 5.83 (s, 2H), 5.49 (s, 2H), 3.97 (t, $J = 6.8$ Hz, 4H), 2.03 (m, 4H), 1.69 (m, 4H), 1.50 (m, 8H), 1.03 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.8, 144.9, 144.8, 142.4, 133.3, 125.7, 125.6, 123.9, 123.8, 116.5, 75.9, 54.1, 48.2, 32.1, 30.8, 26.2, 23.0, 14.4. HRMS calcd for $C_{50}H_{48}O_2$ (M^+): 680.3649; found: 680.3667.

***exo*-5,16(1′,2′)-Benzeno-6,15-epoxy-7,14-dihexyloxy-5,5a,6,15,15a,16-hexahydropentacene (12).** A mixture of **5** (88 mg, 0.20

mmol) and anthracene (86 mg, 0.48 mmol) in xylene (5 mL) was refluxed at 140 °C for 3 h. The solvent was then removed in vacuo, and the residue was chromatographed on silica gel with CH_2Cl_2:hexane (1:2, v/v, slowly up to 1:1), affording product as a colorless solid (100 mg, 81%); mp 77−79 °C. ^1H NMR (400 MHz, $CDCl_3$): 8.66 (s, 2H), 8.03 (dd, J = 6.4, 3.2 Hz, 2H), 7.49 (dd, J = 6.8, 3.2 Hz, 2H), 7.42 (dd, J = 5.2, 3.2 Hz, 2H), 7.33 (dd, J = 5.2, 3.2 Hz, 2H), 7.26 (dd, J = 5.6, 3.2 Hz, 2H), 7.09 (dd, J = 5.6, 3.2 Hz, 2H), 5.40 (s, 2H), 4.58 (s, 2H), 4.26 (m, 4H), 2.62 (s, 2H), 2.03 (m, 4H), 1.71 (m, 4H), 1.52 (m, 8H), 1.06 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 141.5, 141.1, 131.5, 129.4, 128.5, 127.7, 126.3, 126.0, 125.6, 124.1, 123.8, 121.6, 80.1, 73.9, 49.6, 47.7, 31.9, 30.5, 26.1, 22.9, 14.4. HRMS calcd for $C_{44}H_{46}O_3$ (M^+): 622.3442; found: 622.3422.

5,16(1′,2′)-Benzeno-7,14-dihexyloxy-5,16-dihydrohexacene (13). A mixture of **12** (0.10 g, 0.16 mmol), pyridinium *p*-toluenesulfonate (0.40 g, 1.6 mmol), and acetic anhydride (5 mL) was stirred at 120 °C for 13 h. After cooling the mixture to room temperature, the yellow precipitate was collected by filtration and washed thoroughly with methanol (30 mg). The filtrate was concentrated and chromatographed on silica gel with CH_2Cl_2:hexane (1:4, v/v), leading to the second fraction of product as a yellow solid (30 mg) (total yield = 62%); mp 150−152 °C. ^1H NMR (400 MHz, $CDCl_3$): 8.82 (s, 2H), 8.15 (s, 2H), 8.00 (dd, J = 6.4, 3.2 Hz, 2H), 7.49 (dd, J = 5.2, 3.2 Hz, 4H), 7.39 (dd, J = 6.8, 3.2 Hz, 2H), 7.09 (dd, J = 5.6, 3.2 Hz, 4H), 5.57 (s, 2H), 4.19 (t, J = 6.8 Hz, 4H), 2.13 (m, 4H), 1.75 (m, 4H), 1.51 (m, 8H), 1.03 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 147.3, 144.1, 140.5, 131.1, 128.8, 126.0, 125.5, 124.9, 124.1, 123.1, 121.4, 116.0, 76.1, 53.9, 32.1, 30.9, 26.2, 23.0, 14.4. HRMS calcd for $C_{44}H_{44}O_2$ (M^+): 604.3336; found: 604.3360.

Synthesis of Polymer P1. *Procedure for Melt Polymerization.* Monomer **5** (160 mg, 0.36 mmol) was heated at 160 °C under Ar for 3 days. After cooling, the mixture was dissolved in THF (∼1 mL), and the product was precipitated into methanol. The precipitate was collected by centrifuge, washed with methanol, and dried in a vacuum, leading to a white solid as product (150 mg, M_n = 5400 Da, PDI = 1.9).

General Procedure for Solution State Polymerization under High Pressure. Under a nitrogen atmosphere in a glovebox, a solution of **5** (130 mg) in THF (0.33 mL, 0.88 M) was transferred into a short Teflon tube (inner diameter = 5 mm), which was sealed by insertion of two glass rods at its ends. The sealed tube was placed into the hypobaric reactor, which was equipped with a thermocouple and a pressure measuring system. The reaction was carried out under a pressure of 139 600 psi at 145 °C for 5 h. After cooling, the reaction mixture was added dropwise to 10 mL of methanol, leading to the precipitation of a white solid material. The white precipitate was collected by a centrifuge, washed with methanol, and dried in a vacuum (110 mg, 85%, M_n = 9400 Da, PDI = 2.7). ^1H NMR (500 MHz, $CDCl_3$): 6.70−7.32 (m, br, 4H), 4.90 (br, 2H), 4.59 (br, 2H), 3.84 (br, 4H), 2.22 (br, 2H), 2.00 (br, 2H), 1.78 (br, 4H), 1.41 (br, 12H), 0.98 (br, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 144.4, 142.9, 142.2, 136.1, 133.4, 125.8, 123.6, 80.0, 74.6, 48.7, 41.3, 31.9, 30.4, 26.1, 22.9, 14.3.

Synthesis of Polymer P2. *General Procedure of the Dehydration of **P1**.* A mixture of **P1** (100 mg, M_n = 16 400 Da, PDI = 3.63), pyridinium *p*-toluenesulfonate (580 mg), and acetic anhydride (9 mL) was stirred under Ar at 130 °C for 23 h. After cooling to room temperature, a light yellow solid precipitated. The precipitate was collected by filtration, washed thoroughly with methanol, and dried in a vacuum, affording a light yellow solid as crude product (84 mg, 87%). Further purification involved the precipitation of a THF solution in methanol, and the solid was collected by centrifuge and dried in a vacuum (M_n = 16 300 Da, PDI = 2.5). ^1H NMR (500 MHz, $CDCl_3$): 7.93 (br, 2H), 7.36 (br, 2H), 6.95 (br, 2H), 5.88 (br, 2H), 3.93 (br, 4H), 2.02 (br, 4H), 1.70 (br, 4H), 1.52 (br, 8H), 1.06 (br, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.8, 144.3, 141.7, 132.7, 126.0, 125.8, 123.9, 116.6, 75.9, 48.1, 32.1, 30.8, 26.3, 23.0, 14.4.

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Supporting Information Available: ^{13}C DEPT and $^1H-^{13}C$ HMBC NMR spectra of **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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