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Synthesis and Properties of Poly(*p*-phenylene Octylene)

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ABSTRACT: Acyclic diene metathesis (ADMET) polymerization was used as a new synthetic route to a class of processable, hydrophobic, and crystalline polymers which contain only aromatic and aliphatic hydrocarbon units in their backbone. Poly(*p*-phenylene octylene) (**PPPO**), as a first example, was prepared by the ADMET polymerization of 1,4-bis(pent-4-ene)benzene, followed by the catalytic reduction of the resulting unsaturated polymer. The weight-average molecular weights of the polymers obtained with this method were in the range of 13 000−25 000. Poly(*p*-phenylene octylene) was found to be highly soluble in common solvents and to have a melting temperature of around 90 °C, which enabled melt processing into fibers and films without decomposition. Wide-angle X-ray diffraction and annealing experiments on **PPPO** revealed two different crystal modifications. The polymer, as precipitated from the reaction mixture, predominantly forms the kinetically preferred modification α, while the annealing of pristine **PPPO** almost exclusively leads to the thermodynamically more stable modification β.

I. Introduction

Poly(*p*-xylylene) (PPX), usually formed upon chemical vapor deposition (CVD) polymerization,[1−7] offers a unique matrix of excellent properties that has attracted significant interest in both academic and industrial environments. PPX coatings exhibit outstanding thermal[8−10] and mechanical[11] properties, good solvent resistance, high crystallinity, and bulk barrier properties which are among the best of organic polymeric coatings.[12] Thus, PPX-coatings are attractive materials for use in electronics, medical applications, and optical devices.[12] Although there is ample evidence that several industrial groups had research interest in the PPXs during the 1950s, industrial exploitation was stifled by the obstacle PPX presents to conventional processing technologies. Because PPX is insoluble in most solvents, even at elevated temperatures, it cannot be used for solvent-based coatings; neither can it be cast into films nor spun into fibers from solution.[13] On the other hand, the high melting temperature (424 °C, close to the degration temperature) prevents melt-processing of PPX.[13]

Several conceivable approaches to produce PPX-analogous polymers with an enhanced processibility have been proposed and investigated in the past. The introduction of halogen atoms into the phenylene moiety was found to lower the melting point, but did not lead to a significant improvement of the solubility.[12] Greiner et al. attached phenyl or phenethyl side-chains to the phenylene moieties of the PPX-backbone and obtained soluble PPX-analogous derivatives.[14−17] Unfortunately, these polymers exhibit a dramatically reduced crystallinity—some materials are fully amorphous—and show low melting (around 137 °C) or glass transition temperatures (104 °C).

In contrast to the above concepts that rely on the derivatization of the phenylene moieties, our approach is based on the assumption that the flexibility and, therewith, the processibility, of the polymer chain can be significantly enhanced by increasing the number of methylene units in the polymer backbone.[18] To our knowledge, the only polymer of this series of poly(*p*-phenylene alkylene)s that has been described in the literature before is poly(*p*-phenylene octylene) (**PPPO**). This material was synthesized by Cramer et al. using the Suzuki cross-coupling of hydroborated 1,7-octadiene and diiodobenzene, but, unfortunately, apart from a ^{1}H NMR spectrum, the authors did not disclose any physical data regarding their material.[19,20] Kantor et al. investigated some other related all-hydrocarbon, liquid-crystalline polymers having various numbers of methylene spacers and biphenylene units in the polymer backbone.[21,22] The polymers with even numbers of methylene spacers were reported to be completely insoluble in common organic solvents, and their isotropization temperatures were in the range 153−270 °C. By contrast, the polymers with odd numbers of methylene spacers were soluble in $CHCl_3$ but showed lower isotropization temperatures than polymers comprising an even number of methylene groups. Similar results were obtained with a polymer containing a tolan moiety in the polymer backbone.[23]

In this paper, we report the synthesis of **PPPO** as an example for the series of poly(*p*-arylene alkylene)s, employing the acyclic diene metathesis (ADMET) polymerization of an aromatic diene, followed by the catalytic reduction of the resulting polymer. This method has been recently established as a suitable synthetic route to high-molecular-weight, unsaturated polymers that are perfectly linear and free from branching and other defects.[24−28] ADMET polymerization here is used for the synthesis of a class of hydrophobic, crystalline polymers containing only aromatic and aliphatic hydrocarbon units in their backbone, which we refer to as *alkarotic* polymers. For the purpose of comparison, we also prepared **PPPO** by the Suzuki cross-coupling of hydroborated olefins with aromatic halides as suggested by Cramer et al. [19,20]

II. Results and Discussion

Polymer Synthesis via ADMET Polymerization. The ADMET polymerizations were based on the new monomer 1,4-bis(pent-4-ene)benzene (**1**), having two terminal olefinic functions. **1** was prepared in a one-step method, using the nickel complex catalyzed cross-coupling of 1-pentenylmagnesium bromide with *p*-di-

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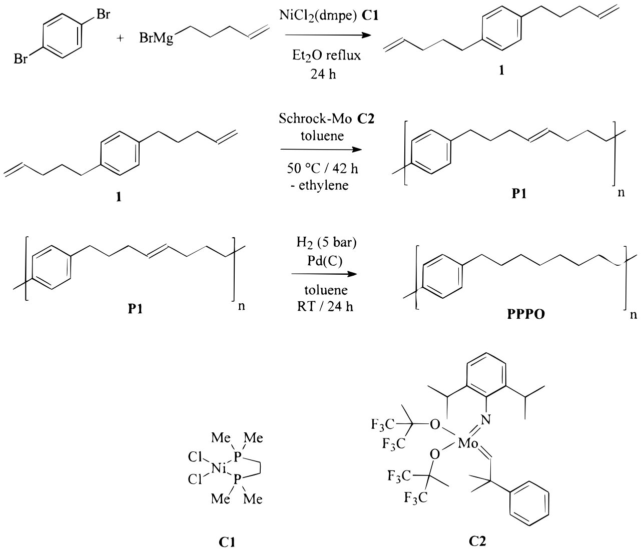
Scheme 1. Monomer Synthesis and Acyclic Diene Metathesis (ADMET) Polymerization



bromobenzene as shown in Scheme 1, according to a general reaction scheme introduced elsewhere.[29,31] The yield of this reaction was found to strongly depend on the type of nickel catalyst used. Best yields of up to 52% were obtained when employing dichloro-{1,2-bis-(dimethylphosphino)ethane}nickel(II) (**C1**) (Scheme 1), which has successfully been used in the past for the preparation of compounds containing olefinic groups.[30] The preparation of this catalyst followed the methods given before.[32,33]

ADMET polymerizations of **1** yield the **PPPO**-precursor polymer **P1** (Scheme 1). ((2,6-Diisopropylphenyl)-imido)neophylidenemolybdenum bis(hexafluoro-*tert*-butoxide) (**C2**)[34] (Scheme 1) was employed as the polymerization catalyst. Typical reaction times were in the range of 48 h; the evolution of ethylene and the increasing viscosity of the reaction mixtures were taken as an indication for the progress of the polymerization. Removal of ethylene from the catalytic equilibrium system under a static vacuum was earlier found to be an effective driving force for the polymerization[25] and, thus, was also applied here. Three different sets of reaction conditions were investigated. In a first method, the polymerization was carried out in bulk (method A); i.e., the catalyst was added to the liquid monomer, and when solidification set in, the reaction mixture was heated, to continue the reaction in the melt. In the second method, the polymerization was also started in bulk, but when the reaction mixture started to solidify, it was redissolved by adding toluene as the solvent (method B). In a third method, the monomer was dissolved in toluene before the catalyst was added, and the entire polymerization was carried out in solution (method C). While no significant difference between the two latter methods was observed, and polymers of comparable molecular weight and molecular weight distribution were obtained, polymerization in bulk (method A) lead to a significantly broader polydispersity ($\bar{M}_w/\bar{M}_n = 7.96$) and a low melting range of the resulting **PPPO** (see below).

The **PPPO**-precursor polymers **P1** were reduced to yield **PPPO**, employing the catalytic hydrogenation with palladium on activated charcoal as the reduction method (Scheme 1).[35] The polymers obtained were characterized to satisfaction by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of polymers **P1** and **PPPO** are shown in Figure 1. The spectra are consistent with the postulated chemical structure, and it is evident that the olefinic signals (5.49−5.36 ppm) have fully disappeared after reduction. All reaction parameters for the ADMET polymerizations and subsequent reductions are compiled in Tables 1 and 2.

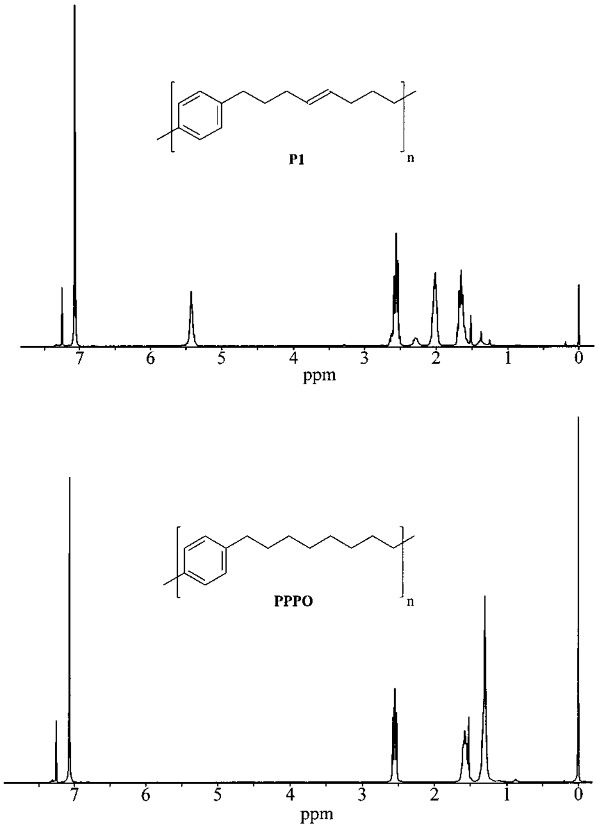


Figure 1. ^{1}H NMR spectra of precursor polymer **P1** (top) and poly(*p*-phenylene octylene) (**PPPO**) (bottom).

Polymer Synthesis via Suzuki Cross-Coupling. For purpose of comparison, **PPPO** was also prepared by the Suzuki cross-coupling of hydroborated 1,7-octadiene (**2**) and diiodobenzene (Method D) as suggested by Cramer et al. (Scheme 2).[19,20] The reaction was carried out in a toluene/THF mixture as the solvent, using two different Pd complexes and a base as the catalyst system. In addition, to improve the molecular weight of the resulting **PPPO**, the asymmetrical monomer 8-(4′-bromophenyl)-1-octene (**3**) was also employed for Suzuki cross-coupling reactions (method E) under otherwise similar conditions (Scheme 2). The use of this asymmetrical monomer represents an improvement of the original route, because limitations with respect to equimolarity of two monomers are eliminated, and the number of condensation steps required to obtain a certain molecular weight is cut in half. All **PPPO** samples prepared by the Suzuki cross-coupling were also satisfactorily characterized by elemental analysis and NMR spectroscopy. Elemental analysis show a slight but systematic offset from the calculated values, in agreement with the presence of a significant amount of end groups. All relevant reaction parameters for the Suzuki polycondensations are summarized in Table 3.

Polymer Characterization. Molecular Weight Analysis. All **PPPO** samples fully and easily dissolved in solvents such as toluene, xylene, benzene, dichlo-

Table 1. ADMET Polymerization: Methods and Results

polymer	method[a]	polymerization temp, °C	reaction time, h	% toluene, w/w	pressure, mbar	mp, °C	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]	yield, %
P1.1	A	50−75	52	66	300−0.04	[b]	15 000	4.3	76
P1.2	B	50	42	42	600	43	n.a.[d]	n.a.[d]	78
P1.3	C	50	42	47	350	41	20 000	5.6	81
P1.4	C	50	42	44	350	51	13 500	4.0	85
P1.5	C	50	2	28	235	44	16 200	4.3	78

[a] Key: A, bulk; B, bulk/solution; C, solution (for details see Experimental Section. [b] Material fully amorphous. [c] Determined by GPC-visco. [d] Not available.

Table 2. PPPO Polymers Produced by Reduction of the ADMET-Precursor Polymers

polymer	method[a]	reaction time, h	% toluene, w/w	mp, °C	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	yield, %
PPPO.1	A	72	98	46−77	25 700	7.9	97
PPPO.2	B	24	99	95	1 300	1.4	56
PPPO.3	C	24	98	82	14 800	2.2	69
PPPO.4	C	24	98	78	15 500	3.0	69
PPPO.5	C	24	98	79	18 000	3.3	98
PPPO.6	C	24	98	82	18 500	3.8	98
PPPO.7	C	24	98	98	6 600	2.5	90
PPPO.8	C	24	98	99	7 500	2.2	50
PPPO.9	C	24	98	90	13 900	3	73

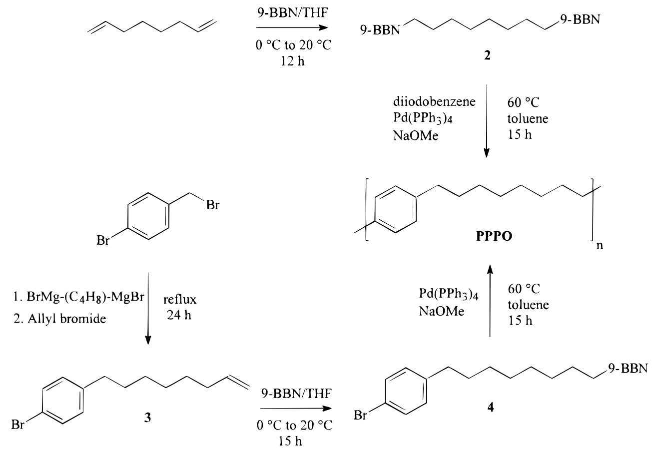
[a] Refers to the method used for the preparation of the unsaturated prepolymer **P1** (cf. Table 1). [b] Determined by GPC-visco.

Table 3. Suzuki Polymerization: Methods and Results

polymer	method[a]	polymerization temp, °C	reaction time, h	% toluene, w/w	$\bar{M}_n$[b]	mp, °C	yield, %	base	catalyst	9-BBN[g] ratio
PPPO.10	D	60	15	96.7	380	43	86	KOH[f]	$Pd(PPh_3)_4$	1
PPPO.11	D	60	16	96.7	1300	91	94	KOH[f]	$Pd(PPh_3)_4$	1
PPPO.12	D	60	18	96.4	1500	96	71	KOH[f]	$PdCl_2(dppf)$	1
PPPO.13	D	80	15	96.8	560	57	86	NaOEt	$Pd(PPh_3)_4$	1
PPPO.14	D	60	14	97.5	560	50	51	NaOMe	$Pd(PPh_3)_4$	1
PPPO.15	D	60	15	96.8	1100	84	73	NaOMe	$Pd(PPh_3)_4$	1
PPPO.16	D	60	18	96.3	1100	85	61	NaOMe	$Pd(PPh_3)_4$	1
PPPO.17	D	60	18	96.7	1500[c]	91	54	NaOMe	$Pd(PPh_3)_4$	1.1
PPPO.18	D	60	96	96.8	1880	93	66	NaOMe	$Pd(PPh_3)_4$	1.1
PPPO.19	E	60	24	96.7	3200[d]	93	47	NaOMe	$Pd(PPh_3)_4$	1.1
PPPO.20	E	60	24	96.8	3400[e]	94	69	NaOMe	$Pd(PPh_3)_4$	1.1

[a] Key: D, polymerization of **2** and diiodobenzene; E, polymerization of **4** (for details see Experimental section). [b] Determined by ^{1}H NMR end group analysis. [c] $\bar{M}_w$(GPC-visco) = 2000; $\bar{M}_w/\bar{M}_n$ = 1.89. [d] $\bar{M}_n$(VPO) = 4500; $\bar{M}_w$(GPC-visco) = 9300; $\bar{M}_w/\bar{M}_n$ = 4.14. [e] $\bar{M}_w$(GPC-visco) = 3500; $\bar{M}_w/\bar{M}_n$ = 2.30. [f] Aqueous solution (10 M). [g] Ratio 9-BBN/olefinic group.

Scheme 2. Monomer Synthesis and Suzuki Cross-Coupling Polymerization



romethane, $CHCl_3$, or THF under ambient conditions and, thus, exhibited the desired improved solubility. Molecular weight data were obtained using ^{1}H NMR−end group analysis for oligomers and gel permeation chromatography (GPC) for polymers. All molecular weight data are given together with the reaction conditions in Tables 1 and 2 for polymers prepared by ADMET polymerization and Table 3 for polymers prepared by Suzuki cross-coupling. The weight-average molecular weights $\bar{M}_w$ obtained with ADMET are in the range of 13 000−25 000, with polydispersities of typically between 2 and 3 and are, thus, in the typical molecular weight regime available with ADMET reactions.[24−28] The molecular weights of **PPPO**s prepared by Suzuki cross-coupling were significantly lower; the maximum number average molecular weights obtained were below 3200. The use of the asymmetric monomer **3**, as suggested here, was found to lead to a significantly improved molecular weight when compared to the standard route.

Thermal Properties and Morphology. The thermal properties of the polymers were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at heating rates of 10 °C/min. TGA experiments revealed that **PPPO** is remarkably stable under dynamic heating: up to around 350 °C under nitrogen atmosphere, as well as in air (Figure 2).

The DSC traces (Figure 3) for the **PPPO**s show well-defined melting ranges between 55 and 100 °C, indicative of a significant crystallinity of these polymers. The graphic representation of the influence of the degree of polymerization (DP) on the melting temperature of the **PPPO**s reveals an interesting behavior (Figure 4). As expected, the peak melting temperature initially increases with increasing DP before leveling off at a

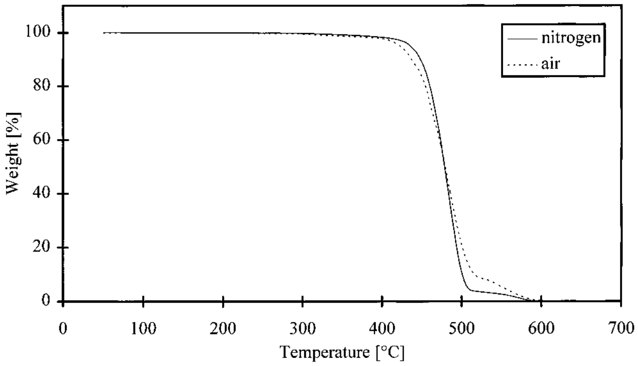


Figure 2. Thermogravimetric analysis of **PPPO.1** under nitrogen and air.

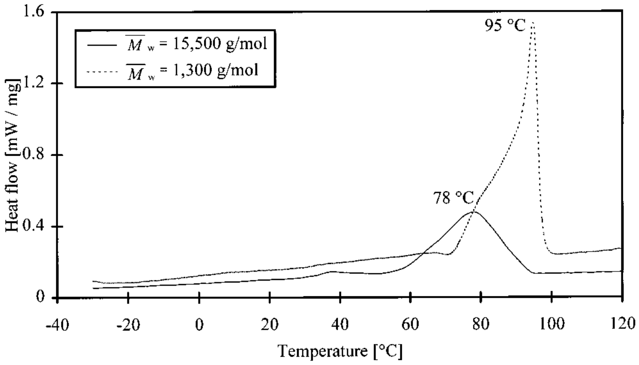


Figure 3. Differential scanning calorimetry of low-molecular weight (**PPPO.2**, $\bar{M}_w$ = 1300) and high-molecular weight (**PPPO.4**, $\bar{M}_w$ = 15 500) **PPPO**.

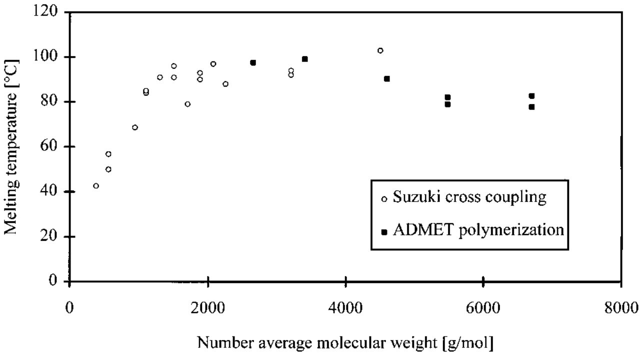


Figure 4. Melting temperatures of **PPPO** for different degrees of polymerization.

temperature of about 100 °C at a number average molecular weight $\bar{M}_n$ of about 2000 (DP $\approx$ 10). However, at $\bar{M}_n$ of about 5000 (DP $\approx$ 25), a significant drop of the melting temperature to a new plateau value of about 80 °C was observed. In addition, as can be seen in Figure 3, the shape of the endothermic melt transition changes from a fairly narrow, well-resolved peak to a significantly broader signal. This behavior can be related to different causes. For example, the observed effect is consistent with a possible change from melting of extended chain to folded chain crystals, as is well-documented for, e.g., polyethylene in a comparable molecular-weight regime.[36] The observed behavior could also relate to the existence of different crystal structures; in fact, polymorphism is well-known to occur in the case of PPX.[11,37,38]

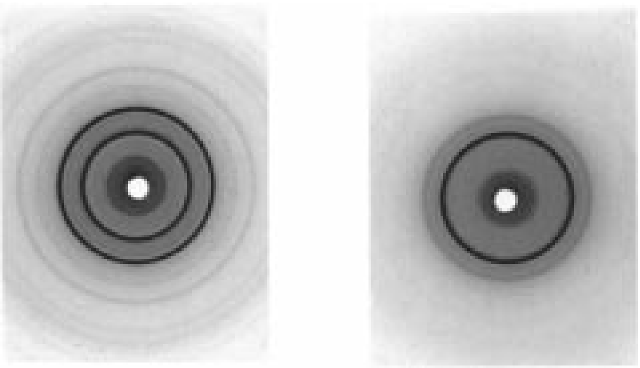


Figure 5. Wide-angle X-ray diffraction patterns of **PPPO** of modification α (left) and modification *β* (right).

To investigate the thermal behavior of **PPPO** in more detail, thermal annealing experiments, combined with wide-angle X-ray diffraction (WAXD) experiments, were carried out. WAXD patterns of all *pristine* **PPPO** samples (independent of the molecular weight and the method of preparation) are identical and show a significant crystallinity (Figure 5). A (weak) reflection corresponding to the largest spacing is found at 11.9 Å. This value represents the distance between the polymer repeat units and is in good agreement with the one calculated from standard bond lengths and angles (12.5 Å).[39] In addition, the diffractograms of *pristine* **PPPO** show prominent reflections at 5.2 and 3.7 Å, which we found to be characteristic for a crystal structure that we designate as modification α. When the same polymers were molten under inert atmosphere for 60 min and subsequently *annealed* for 48 h at 75 °C, the WAXD patterns (also shown in Figure 5), show the most prominent reflection at 4.5 Å, which we found characteristic for a crystal structure that we designate as modification *β*. While the reflection corresponding to the largest spacing at 11.9 Å remained unchanged in the latter, the reflections at 5.2 and 3.7 Å disappeared almost completely. These observations suggest that virgin **PPPO**, as precipitated from the reaction mixture, apparently predominantly forms a crystal structure of the α-form, while the annealing of pristine **PPPO** almost exclusively leads to the *β*-modification. We therefore conclude, that modification α is kinetically preferred, while modification *β* is of higher thermodynamic stability. Independent of the molecular weight, it is therefore possible to selectively generate **PPPO** of the desired crystal modification. Samples of the different crystal modifications did not display significantly different thermal behavior. Hence, we attribute the above referred melting temperature/chain length development to the standard transition of melting of extended chain crystals to that of folded chain crystals.

Finally, it is noteworthy that **PPPO** samples of a $\bar{M}_w$ higher than about 14 000 have excellent fiber- and film-forming properties.

III. Conclusions

We have demonstrated that acyclic diene metathesis polymerization can be used as an efficient synthetic route to a class of processable, hydrophobic, and crystalline polymers which contain only aromatic and aliphatic hydrocarbon units in their backbone (alkarotic polymers). Poly(*p*-phenylene octylene), as a first example, was prepared by the ADMET polymerization of 1,4-bis-(pent-4-ene)benzene, followed by the catalytic reduction of the resulting unsaturated polymer. The weight-average molecular weight of the polymers obtained with this method were in the range 13 000−25 000, significantly higher than **PPPO,** which, for the purpose of comparison, was prepared by the Suzuki cross-coupling of hydroborated olefins and aryl halogenides.

Wide-angle X-ray diffraction and annealing experiments on **PPPO** revealed two different crystal modifications. The polymer, as precipitated from the reaction mixture, predominantly forms the kinetically preferred modification α, while the annealing of pristine **PPPO** almost exclusively leads to the thermodynamically more stable modification β.

All **PPPO** samples prepared in this work are highly soluble in common solvents; the low melting temperature enabled melt processing into homogeneous fibers and films. Future work designated to generate melt-processable PPX-analogous polymers, is focused on adjusting the number of CH_2 spacers in order to cause the melting temperature to be in the range of about 200−250 °C.

IV. Experimental Section

General Data. All reagents and solvents were purchased from Fluka, Aldrich Chemical Co. and Merck. Catalyst **C2** was purchased from Strem Chemicals, Inc. All experiments were carried out under a nitrogen or argon atmosphere by applying standard Schlenk, vacuum-line or glovebox techniques. All ADMET polymerizations were carried out in a glovebox, under an N_2 atmosphere with water and oxygen concentrations lower than 1 ppm. A stationary vacuum was used for the polymerizations. DSC and TGA measurements were performed on Netzsch CC 200 and Netzsch TG 209 instruments. ^1H NMR and ^{13}C NMR spectral data are expressed in ppm relative to internal TMS and were obtained on various Bruker NMR spectrometers. GPC measurements were performed on a Knauer GPC (detectors: differential refractometer Knauer, Viscotek H502 differential-viscosimeter; conditions: flow 1.1 mL/min, solvent tetrahydrofuran, 45 °C). Elemental analyses and mass spectra were carried out by the Microanalysis and Mass Spectra Laboratories of the Department of Chemistry of ETH Zürich. Wide-angle X-ray diffraction experiments were performed with a Seifert ISO-Debeyflex 2002, using Ni-filtered Cu Kα radiation as the ray source (conditions: 12 h, 30 mA, 35 kV).

Purification of Monomers, Reagents, and Solvent. Due to the very high sensitivity of the ADMET catalyst, all chemicals used in conjunction with this catalyst were of the utmost purity. Monomer **1** was purified by column chromatography, dried over calcium hydride for 24 h, distilled onto molecular sieves (4 Å), and subsequently deoxygenated by sparging with Ar for at least 2 h prior to use. We used ^1H NMR and elemental analysis to verify the purity of the monomer. The absence of water was confirmed by the observation of a persistent purple color, after a sodium/benzophenone indicator solution was added to the monomer.

Catalyst Synthesis. Dichloro-{1,2-bis(dimethylphosphino)ethane}nickel(II) (C1) ($NiCl_2$(dmpe)).[32,33] A solution of $NiCl_2(H_2O)_6$ (661 mg, 2.781 mmol) in ethanol (5 mL) was added to a stirred solution of 1,2-bis(dimethylphosphino)ethane (850 mg, 5.661 mmol) in ethanol (14 mL). After concentration of the resulting mixture to low volume and the addition of a mixture of acetone (14 mL)/toluene (28 mL), orange crystals precipitated which were filtered off, dried, and redissolved in ethanol (14 mL). A second portion of $NiCl_2(H_2O)_6$ (1.074 g, 4.521 mmol) in ethanol (18 mL) was added to this latter solution, and the reaction mixture was stirred for 90 min at 85 °C. The resulting precipitate was collected and recrystallized from ethanol to yield gold-red **C1** (810 mg, 2.90 mmol, 51%). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.75−1.73 (m, 4H, CH_2), 1.70−1.54 (m, 12H, CH_3). ^{31}P NMR (300 MHz, $CDCl_3$, 298 K): δ 50.86 (s, 2P). Anal. Calcd for $NiC_6H_{16}P_2Cl_2$: C, 25.76; H, 5.76; P, 22.15; Cl, 25.35. Found: C, 25.95; H, 5.51; P, 22.37; Cl, 25.50.

Monomer Synthesis. 1,4-Bis(pent-4-ene)benzene (1). 1-Pentenylmagnesium bromide was prepared by reacting 5-bromopent-1-ene (9.58 g, 64.26 mmol) and magnesium turnings (1.73 g, 71.03 mmol) in absolute diethyl ether (60 mL) for 150 min at room temperature. The remaining solids were filtered off, and the solution was added dropwise to a stirred mixture of *p*-dibromobenzene (6.07 g, 25.74 mmol), $NiCl_2$(dmpe) (90.3 mg, 0.32 mmol) and diethyl ether (20 mL) at room temperature and the resulting mixture was refluxed for 24 h at 35 °C. Another portion of $NiCl_2$(dmpe) (30.9 mg, 0.11 mmol) was added to the reaction mixture which was then allowed to reflux for another 6 h. Finally, the reaction was quenched with aqueous HCl (2 N, 125 mL), the organic phase was separated off and washed with water (3 × 50 mL), and the aqueous layer was extracted with diethyl ether (3 × 80 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. Column chromatography (silica gel 60, *n*-hexane) of the resulting oil yielded **1** (2.87 g, 52%) as a colorless oil; bp 58 °C (7.5×10^{-2} mbar). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.08 (s, 4H, Ar), 5.90−5.77 (m, 2H, C═CH), 5.06−4.94 (m, 4H, $C{=}CH_2$), 2.59 (t, J_{HH} = 7.75 Hz, 4H, $Ar{-}CH_2$), 2.13−2.05 (m, 4H, $CH_2{-}CH{=}CH_2$), 1.75−1.65 (m, 4H, $C{-}CH_2{-}C$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 139.96 (s, 2C, Ar−C), 138.70 (s, 2C, $C{=}CH_2$), 128.36 (d, 4C, Ar), 114.64 (t, 2C, $H_2C{=}C$), 34.93 (t, 2C, C−C═C), 33.35 (t, 2C, C−Ar), 30.70 (t, 2C, $C(CH_2)_2$). Mass spectrum: *m/e* 214 (M^+ parent). Anal. Calcd for $C_{16}H_{22}$: C, 89.66; H, 10.34; Found: C, 89.58; H, 10.17.

8-(4′-Bromophenyl)-1-octene (3).[40] A solution of 1,4-bis(bromomagnesio)butane in diethyl ether (40 mL), which was prepared from 1,4-dibromobutane (16.343 g, 75.693 mmol) and magnesium turnings (18.397 g, 0.757 mol), was added to a solution of 4-bromobenzyl bromide (9.459 g, 37.847 mmol) in diethyl ether (20 mL) at 0 °C. After being stirred for 4.5 h at 0 °C, the reaction mixture was cooled to −40 °C and a solution of allyl bromide (12.81 mL, 0.151 mol) in diethyl ether (20 mL) was slowly added such that the temperature of the reaction mixture was kept between −45 and −60 °C. After the addition was complete, the mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched with water; the mixture was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. Column chromatography (silica gel 60, *n*-hexane) of the resulting yellow oil yielded a 10/14-mixture (5.0 g) of 4-(4′-bromophenyl)-1-butene and **3**. Pure **3** (1.8 g, 18%) was obtained by vacuum distillation. bp 80−85 °C (4.0×10^{-2} mbar). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.38 (d, J = 8.34, 2H), 7.03 (d, J = 8.20, 2H), 5.86−5.73 (m, 1 H), 5.02−4.90 (m, 2H), 2.55 (t, J = 7.47, 2H), 2.06−2.00 (m, 2 H), 1.63−1.53 (m, 2 H), 1.41−1.26 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 141.74 (Ar), 139.04 ($-HC{=}CH_2$), 131.25 (Ar), 130.15 (Ar), 119.27 (Ar), 114.24 ($-CH{=}CH_2$), 35.31, 33.74, 31.24, 29.00, 28.91, 28.81 (all CH_2). Anal. Calcd for $C_{14}H_{19}Br$: C, 62.93; H, 7.17. Found: C, 62.83; H, 7.39.

Polymer Synthesis by ADMET Polymerization. Method A: Bulk Polymerization. Poly(*p*-phenylene oct-4-enylene) (P1.1). **C2** (10.0 mg, 0.013 mmol) was added to rapidly stirred 1,4-bis-(pent-4-ene)benzene (**1**) (472.0 mg, 2.20 mmol) at 50 °C. The resulting yellow mixture started to vigorously evolve gas (ethylene). After about 5 min, the evolution of gas decreased, a dynamic vacuum of about 200 mbar was established, and the reddish reaction mixture became highly viscous. After 60 min, the temperature was increased to 75 °C and a second portion of catalyst **C2** (4 mg, 5.2 μmol) was added, enhancing the evolution of gas, now under a further reduced pressure (0.04 mbar). After 7 h, toluene (0.93 g) and **C2** (7 mg, 9.1 μmol) were added to the highly viscous reaction mixture and the reaction was continued for another 45 h. After a total reaction time of 52 h the dark viscous solution was diluted with another portion of toluene (2 mL) and precipitated into methanol (50 mL). Polymer **P1.1** (310 mg, 76%) was obtained as a dark, waxy material. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 4H, Ar), 5.44−5.37 (m, 2H, −CH═CH-), 2.65−2.51 (m, 4H, $Ar{-}CH_2$), 2.02−2.01 (m, 4H, $C_2{-}CH{=}CH_2$), 1.68−1.63 (m, 4H, CH_2). ^{13}C NMR (75

MHz, $CDCl_3$, 298 K): δ 139.80 (Ar), 130.37 (HC=CH), 128.30 (Ar), 34.94, 32.18, 31.37 (all CH_2). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; Found: C, 90.20; H, 9.81. GPC: $\bar{M}_w$ = 15 000; $\bar{M}_w/\bar{M}_n$ = 4.27.

Method B: Bulk/Solution Polymerization. Poly(*p*-phenylene oct-4-enylene) (P1.2). **C2** (10.0 mg, 0.013 mmol) was added to rapidly stirred 1,4-bis-(pent-4-ene)benzene (**1**) (480.0 mg, 2.52 mmol) at room temperature. The resulting yellow solution started to vigorously evolve gas (ethylene). After about 5 min, the reaction mixture solidified and was redissolved in toluene (350 mg) and heated to 50 °C. A second portion of catalyst **C2** (6 mg, 0.008 mmol) was added, enhancing the evolution of gas, now under a reduced pressure (600 mbar). After 15 min, the solution turned red and the evolution of gas stopped slowly. A third portion of catalyst **C2** (7.5 mg, 0.010 mmol) was added, and the vacuum was lowered to 350 mbar. After a total reaction time of 42 h, the highly viscous reaction mixture was precipitated into methanol. Polymer **P1.2** (374.0 mg, 78%) was obtained as an olive-green, waxy material; mp 43 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 4H, Ar), 5.49−5.38 (m, 2H, −CH=CH−), 2.63−2.50 (m, 4H, Ar−CH_2), 2.03−2.01 (m, 4H, CH_2−CH=CH_2), 1.70−1.57 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 139.82 (Ar), 130.39 (HC=CH), 128.31 (Ar), 34.95, 32.19, 31.38 (all CH_2). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; Found: C, 90.24; H, 9.67. GPC: $\bar{M}_w$ = 14 600; $\bar{M}_w/\bar{M}_n$ = 3.60.

Method C: Solution Polymerization. Poly(*p*-phenylene oct-4-enylene) (P1.4). 1,4-Bis(pent-4-ene)benzene (**1**) (571 mg, 2.66 mmol) was dissolved in toluene (446 mg). **C2** (9 mg, 0.012 mmol) was added to the rapidly stirred solution at room temperature. The resulting yellow solution started to vigorously evolved gas (ethylene). After about 5 min, an additional portion of **C2** (8 mg, 0.011 mmol) was added, the reaction temperature was increased to 50 °C, and the pressure was reduced (350 mbar). The solution became dark-red and further evolved ethylene. After 2 h, a third portion of catalyst **C2** (9 mg, 0.012 mmol) was added to the slightly viscous solution. After a total reaction time of 42 h, the reaction mixture was precipitated into methanol (20 mL). Polymer **P1.4** (422.0 mg, 85%) was obtained as an olive-green, waxy material; mp 51 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 4H, Ar), 5.49−5.36 (m, 2H, −CH=CH−), 2.65−2.53 (m, 4H, Ar−CH_2), 2.05−2.01 (m, 4H, CH_2−CH=CH_2), 1.71−1.60 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 139.81 (s, 2C, Ar−C), 130.38 (d, 2C, HC=CH), 128.31 (d, 4C, Ar), 34.95 (t, 2C, C−C=C), 32.19 (t, 2C, C−Ar), 31.38 (t, 2C, C(CH_2)$_2$). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; Found: C, 90.20; H, 10.15. GPC: $\bar{M}_w$ = 13 500; $\bar{M}_w/\bar{M}_n$ = 4.0.

Preparation of PPPO.1 by Reduction of poly(*p*-phenyleneoct-4-enylene) (P1.1). Palladium on charcoal (80 mg, 10% Pd) was added to a solution of **P1.1** (240 mg, 1.28 mmol) in toluene (10 mL), and the reaction mixture was stirred for 72 h under a hydrogen pressure of 5 bar. The catalyst was removed by centrifugation and filtration through a PTFE filter (pore size = 1 μm). Precipitation of the resulting solution into methanol yielded the white polymer **PPPO.1** (235 mg, 97%); mp 46−77 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.06 (s, 4H, Ar), 2.55 (t, $J_{(HH)}$ = 7.7 Hz, 4H, Ar−CH_2), 1.60−1.55 (m, 4H, CH_2−C−Ar), 1.30 (s, 8H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 140.01 (Ar), 128.19 (Ar), 35.54, 31.56, 29.44, 29.37 (all CH_2). Anal. Calcd for $C_{14}H_{18}$: C, 89.30; H, 10.70; Found: C, 89.30; H, 10.83. GPC: $\bar{M}_w$ = 25 700 $\bar{M}_w/\bar{M}_n$ = 7.96.

Polymer Synthesis by Suzuki-Cross-Coupling Polymerization. Method D: Two Symmetrical Monomers. PPPO.18. After adding 9-borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M in THF, 14.9 mL, 7.46 mmol) to 1,7-octadiene (0.3739 g, 3.3929 mmol) at 0 °C, the reaction mixture was allowed to warm to room temperature within 2 h and subsequently stirred at this temperature for another 16 h. The colorless, clear solution was then added to a suspension of diiodobenzene (1.1193 g, 3.3929 mmol), Pd(PPh_3)$_4$ (39.21 mg, 33.93 μmol) and sodium methylate (0.550 g, 10.18 mmol) in toluene (19 mL); the mixture was heated to 60 °C and stirred under reflux for 96 h. After cooling, the reaction mixture was added dropwise into rapidly stirred methanol (250 mL), and after being stirred for 1 h, the precipitated polymer was collected and washed with methanol, H_2O, hot ethanol, acetonitrile and acetone. Drying at room temperature in vacuo overnight yielded **PPPO.18** as an off-white powder (424 mg, 66%); mp 93 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 4H), 2.55 (t, *J* = 7.45, 4H), 1.65−1.54 (m, 4H), 1.40−1.20 (br s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K); δ 140.02 (Ar), 128.20 (Ar), 35.55, 31.56, 29.44, 29.36 (all CH_2). DP_{NMR}: 10. Anal. Calcd for $C_{14}H_{18}$: C, 89.30; H, 10.70; Found: C, 85.80; H, 10.60.

Method E: One Asymmetrical Monomer. PPPO.19. After 9-BBN (0.5 M in THF, 6.5 mL, 3.2 mmol) was added to 8-(4′-bromophenyl)-1-octene (0.7837 g, 2.9329 mmol) at 0 °C, the reaction mixture was allowed to warm to room temperature within 2 h and subsequently stirred at this temperature for another 7 h. The colorless, clear solution was then added to a suspension of Pd(PPh_3)$_4$ (33.89 mg, 29.329 μmol) and sodium methylate (0.2377 g, 4.3994 mmol) in toluene (16 mL), and the mixture was heated to 60 °C and stirred under reflux. After 17 h, another portion of Pd(PPh_3)$_4$ (36.5 mg, 31.586 μmol) was added. After a total reaction time of 24 h, the reaction mixture was cooled and added dropwise into rapidly stirred methanol (175 mL). After being stirred for 1 h, the precipitated polymer was collected and washed with methanol, hot ethanol, acetonitrile, and acetone. Drying at room temperature in vacuo overnight yielded **PPPO.19** as an off-white powder (260 mg, 47%); mp 93 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 4H), 2.55 (t, *J* = 7.51, 4H), 1.60−1.50 (m, 4H), 1.31 (br, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 140.12 (Ar), 128.29 (Ar), 35.63, 31.64, 29.53, 29.45 (all CH_2). GPC: $\bar{M}_w$ = 9600; $\bar{M}_w/\bar{M}_n$ = 4.14. DP_{NMR}: 17. Anal. Calcd for $C_{14}H_{18}$: C, 89.30; H, 10.70; Found: C, 86.18; H, 11.01.

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