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Poly(*p*-phenylene butylene): A New, Processable, High-Melting Hydrophobic Polymer

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ABSTRACT: With the objective to produce processable, high-melting, hydrophobic, and crystalline polymers, we embarked on the synthesis of poly(*p*-phenylene butylene) (**PPPB**) as a new representative of the class of polymers that contain only aromatic and aliphatic hydrocarbon units in their backbone. Acyclic diene metathesis (ADMET) polymerization of *p*-diallylbenzene followed by catalytic reduction of the resulting unsaturated polymer was used as the primary synthetic route to **PPPB**. For the ADMET polymerizations, Schrock's alkylidene molybdenum complex, Grubbs' benzylidene ruthenium catalyst, and two classical systems ($WOCl_2(OAr)_2/Bu_4Sn$ and WCl_6/Bu_4Sn) were employed, and different reaction conditions were compared. $WOCl_2(OAr)_2/Bu_4Sn$ in refluxing toluene proved to be the most appropriate catalyst system to produce the crystalline and high-melting poly(*p*-phenylene but-2-enylene) precursor polymer in high molecular weight and chemically pure form. Catalytic hydrogenation of the latter led to poly(*p*-phenylene butylene) with number-average molecular weights of up to 14 000 g mol^{-1}. The latter polymer was found to have a melting temperature of between 200 and 215 °C and to be highly crystalline and melt-processable. Thus, **PPPB** indeed represents a high-melting, hydrophobic polymer that permits conventional processing technologies as opposed to its "homologue" poly(*p*-xylylene) (PPX).

Introduction

Hydrophobic polymers comprising only aromatic and/or aliphatic moieties in their backbone have been shown to cover an extremely broad spectrum of useful materials properties.[1,2] Poly(*p*-phenylene alkylene)s (Figure 1) are one family belonging to this class of polymers. Materials that represent the limits of this series of polymers are, on one hand, the fully rigid, intractable poly(*p*-phenylene) (PPP; Figure 1: $y = 0$)[2] and the highly flexible, low melting polyethylene (PE) on the other.

Surprisingly, the only well-investigated and commercially exploited polymer from this series other than, of course, polyethylene is poly(*p*-xylylene) (PPX; Figure 1: $y = 2$),[3] which offers a unique matrix of excellent properties,[4,5] including exceptional chemical resistance and extraordinary mechanical[6] and barrier properties.[1] PPX coatings, usually formed through chemical vapor deposition (CVD), find utilization in microelectronics, medicine, and a variety of other applications.[1] However, the limited solubility and the high crystalline melting temperature (427 °C, close to degradation) of PPX prevent conventional melt and solution processing.[7,8]

Driven by the goal to produce crystalline polymeric materials, which combine the outstanding processability of PE and at least some of the unique materials properties of PPX, we undertook to further explore this family of poly(*p*-phenylene alkylene)s, referred to as *alkarotic* polymers.[9] Our approach is based on the notion that adjusting the number of methylene units in the backbone allows control of the flexibility of the polymer chain and, therewith, the melting temperature and processability—a concept that has been successfully applied in the design of both novel hydrocarbon polymers[10−15] and polyamides.[16−18] To our knowledge, the only studies of poly(*p*-phenylene alkylene)s that have been described in the literature were conducted by Cramer and Percec on poly(*p*-phenylene octylene) (**PPPO**)[19,20] and by Brown and Farthing.[21] While Cramer et al. discussed the synthesis of poly(*p*-phenylene octylene) (**PPPO**)—unfortunately without disclosing any physical characteristics—Brown and Farthing described an attempt to produce poly(*p*-phenylene butylene) (**PPPB**) by the Wurtz condensation of 1,4-bis(2-chloroethyl)benzene. The experiments—not reproduced by us—resulted in a material that was reported to be amorphous but (rather inconsistently) to have a melting temperature between 395 and 415 °C, thus in a temperature regime in which thermoplastic processing is still stifled and likely to be accompanied by decomposition. Erroneously guided by the results of Brown and Farthing,[21] we recently synthesized **PPPO** in an attempt to produce a melt-processable poly(*p*-phenylene alkylene). However, to our surprise, this highly crystalline polymer was found to have a melting temperature as low as 90 °C.[9]

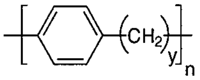

Figure 1. Molecular structure of poly(*p*-phenylene alkylene)s.

Employing a newly developed semiempirical method that allows to calculate the melting temperature of different representatives of homologous classes of polymers,[22] and using the melting temperatures of **PPX** and **PPPO**, we interpolated the melting temperatures of poly(*p*-phenylene hexylene) (**PPPH**; Figure 1: $y = 6$) and **PPPB** (Figure 1: $y = 4$) to be 127 and 202 °C, respectively. On the basis of these estimations, and with the above-discussed technological potential of a high-melting, melt-processable hydrophobic polymer in mind, we revisited the synthesis of **PPPB**. We employed the acyclic diene metathesis (ADMET) polymerization of an aromatic diene, followed by the catalytic reduction of the resulting unsaturated polymer as the primary synthetic route to **PPPB**. This method has been established as a suitable synthetic tool to produce high molecular weight, unsaturated polymers that are perfectly linear and free from branching and other defects.[23]

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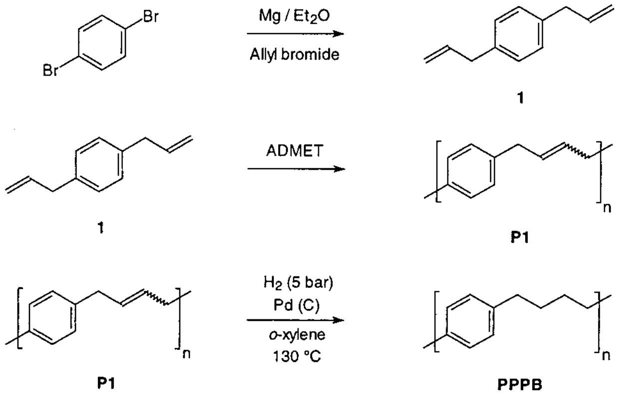
Table 1. ADMET Polymerization: Methods and Results

polymer	catalyst	polym temp, °C	solvent, % w/w	equiv cat.[a]	precip of **P1** after	react. time, h	yield, %	T_m, °C	dp[b]	$\bar{M}_n$[b]	side reactions[c]	% *cis*[d]
P1.A1	**C1**	RT-50	toluene, 0/84[e]	0.0025	30 min	24	42	147	14 ± 1.6	1800	0.05	20
P1.A2	**C1**	RT-50	toluene, 96	0.0025	60 min	24	53	150	14 ± 1.4	1800	0.06	17
P1.A3	**C1**	75	toluene, 89	0.0023	3 h	52	53	162	9.5 ± 1	1200	0.4	30
P1.A4	**C1**	55	TCB, 69	0.0026	9 h	23	58	130	20 ± 2.4	2600	0.08	24
P1.A5	**C1**	60	TCB, 95	0.0046	CRT[f]	94	78	157	14 ± 3	1800	0.5	30
P1.B1	**C2**	110	toluene, 51	0.0023	CRT[f]	6	75	105−136	38 ± 31	4900	0.15	30
P1.C1	**C3**	100	toluene, 0/86[e]	0.002	10 min	18	73	178	20 ± 1.6	2600	0	20
P1.C2	**C3**	105	toluene, 28	0.0032	5 min	7	98	184	47 ± 6	6100	0	19
P1.C3	**C3**	107	toluene, 58	0.0072	12 min	4	98	182	30 ± 2.2	3900	0	14
P1.C4	**C3**	97	toluene, 93	0.0024	1 h	6	88	191	40 ± 0.5	5200	0	15
P1.C5	**C3**	110	toluene, 91	0.0032	3 h	20	90	193	42 ± 6	5500	0	18
P1.C6	**C3**	reflux	toluene, 89	0.0035	5 h	15	93	186	n.a.[k]	n.a.[k]	0	20
P1.C7	**C3**	100	TCB, 92	0.002	CRT[f]	31	93	180	12.4± 1	1600	0	21
P1.C8	**C3**	105	*o*-xylene, 93	0.0044	10 h	31	85	181	17 ± 1.5	2200	0	19
P1.C9	**C3**	125	*o*-xylene, 94	0.0024	CRT[f]	30	84	177	56 ± 16	7300	0.02	21
P1.C10	**C3**	125	*o*-xylene, 66	0.0022	4 h	22	94	178	62 ± 12	8000	0.06	22
P1.C11[g]	**C3**	130	*o*-xylene, 93	0.0084	n.a.[h]	48	54	*i*	*i*	*i*	*i*	*i*
P1.D1	**C4**	130	*o*-xylene, 66	0.028	n.a.[h]	52	92	*i*	*i*	*i*	*i*	*i*

[a] Referring to the amount of monomer. [b] Degree of polymerization dp or number-average molecular weight $\bar{M}_n$, respectively, determined by ^{1}H NMR end group analysis. [c] Arbitrarily evaluated by the ratio of arylvinylic protons per internal olefinic protons in the ^{1}H NMR spectrum. [d] Fraction of *cis* configuration of the olefinic groups as determined by ^{1}H NMR measurements. [e] Start of the polymerization in the bulk, addition of solvent after 1 h (**P1.A1**) and after 10 min (**P1.C1**), respectively. [f] CRT: cooling reaction mixture to room temperature. [g] Postcondensation of **P1.C5**. [h] Not available. [i] Material insoluble and not meltable. [k] No end groups detectable in ^{1}H NMR spectrum due to high degree of polymerization.

Scheme 1. Monomer Synthesis, Acyclic Diene Metathesis (ADMET) Polymerization, and Catalytic Reduction of the Unsaturated Precursor Polymer P1



This method also was successfully applied in our earlier synthesis of **PPPO**.[9] For the purpose of comparison, we also prepared **PPPB** by the Suzuki cross-coupling of a hydroborated olefin with an aromatic halide.[9,19,20,24,25]

Results and Discussion

Polymer Synthesis via ADMET Polymerization. All ADMET polymerizations were based on *p*-diallylbenzene (**1**), which was prepared in the two-step, one-pot procedure shown in Scheme 1, adapting a general method described elsewhere.[26] ADMET polymerization of **1** yielded the unsaturated **PPPB**-precursor polymer **P1** (Scheme 1). Four ADMET catalyst systems in various solvents, utilized at different temperatures, were investigated in this work (see Table 1 and Experimental Section): Schrock's 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(hexafluoro-*tert*-butoxide) (**C1**), Grubbs' bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (**C2**), and the classical tungsten systems *trans*-dichlorobis(2,6-dibromophenoxy)oxotungsten(VI)/Bu$_4$Sn (**C3**) and tungsten(VI) chloride/Bu$_4$Sn (**C4**) shown in Figure 2.

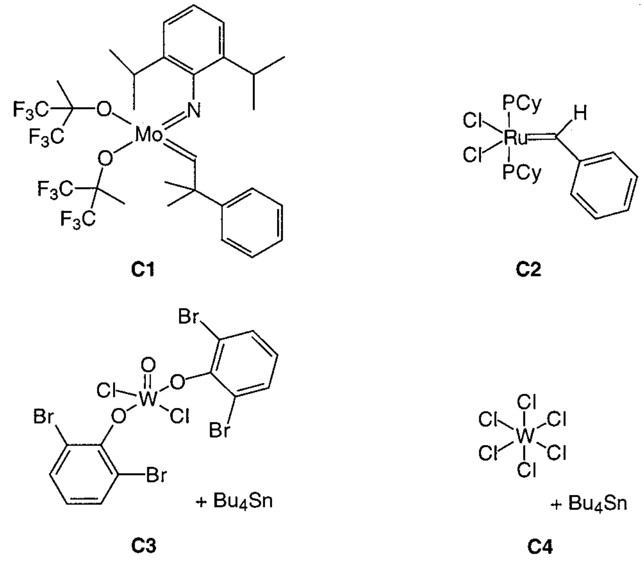


Figure 2. ADMET catalyst systems employed in this work: 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(hexafluoro-*tert*-butoxide) (**C1**), bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (**C2**), *trans*-dichlorobis(2,6-dibromophenoxy)oxotungsten(VI)/Bu$_4$Sn (**C3**), and tungsten(VI) chloride/Bu$_4$Sn (**C4**).

In a first series of ADMET polymerizations of **1**, we used Schrock's alkylidene molybdenum complex **C1**, which we successfully applied in the earlier synthesis of **PPPO**.[9] Bulk polymerization of **1** was hampered by the relatively high crystalline melting temperature (cf. Figure 6) of the precursor polymer **P1** (see Table 1, **P1.A1** and **P1.C1**), resulting in premature precipitation of **P1**, which occurred typically within several minutes after the polymerization was initiated. Consequently, only low-molecular weight materials were obtained under these conditions. Therefore, all subsequent polymerizations were conducted in solution and at elevated temperatures (Table 1). However, also when conducting the polymerization with **C1** at temperatures of 55 °C and changing the solvent to 1,2,4-trichlorobenzene (TCB) (which appeared to be a slightly better solvent for **P1** than toluene), early precipitation of **P1** was observed, leading to polymers of relatively low molecular

Table 2. Poly(*p*-phenylene butylene) Prepared by Reduction of the ADMET-Precursor Polymers P1

polymer	P1[a]	reduction temp, °C	solvent, % w/w	reaction time, h	conversion, %	yield, %	T_m, °C	$\bar{M}_n$[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
PPPB.1	**P1.A1**	100	toluene, 99.5	24	100	68	160–175[d]	1800	1200[e,f]	n.a.[f]
PPPB.2	**P1.C8**	125	*o*-xylene, 99.7	48	99.2	93	170–200	2200	4000	2.1
PPPB.3	**P1.C2**	125	*o*-xylene, 99.7	50	99.5	81	180–225	6200	11000	1.8
PPPB.4	**P1.C6**	120	*o*-xylene, 99.7	72	98.6	50	195–215	n.a.[g]	26000	3.0

[a] Refers to the polymer in Table 1 that was reduced to produce the corresponding **PPPB**. [b] Determined by ^{1}H NMR end group analysis of the precursor polymer **P1**. [c] Determined by HT-GPC. [d] Low T_m because of low $\bar{M}_n$. [e] Determined by ^{1}H NMR end group analysis. [f] HT-GPC not available because of low $\bar{M}_n$. [g] No end groups detectable in ^{1}H NMR spectrum.

weights (see Table 1, **P1.A4**). Further increase of the reaction temperature to 60 or 75 °C resulted in a color change of the reaction mixture from red to dark brown and a reduction in molecular weight of the products, indicating the decomposition of catalyst **C1** (see Table 1, **P1.A3** and **P1.A5**). In addition to the rapidly decreasing activity of **C1** under those conditions, signals related to a significant fraction of arylvinylic protons were observed in the ^{1}H NMR spectra of the respective polymers **P1.A3** and **P1.A5**, indicating the emergence of unwanted side reactions. Thus, the thermal stability of the Schrock Mo catalyst **C1**, under the employed conditions, appeared to be limited to temperatures below about 60–70 °C, which is in excellent agreement with results of Wagener et al.,[27] who reported decomposition of **C1** to occur in the temperature range 65–75 °C.

Hence, in view of the inherent, limited solubility of **P1** at low temperatures—which arises from the rigidity of its backbone and the lack of favorable enthalpic interactions with solvents—and in order to avoid early precipitation of the polymer **P1** during polymerization, use of a catalyst that is stable at significantly higher temperatures appeared to be a prerequisite. In experiments with Grubbs' ruthenium catalyst **C2** at 110 °C (see Table 1, **P1.B1**, and Experimental Section) the initially lively evolution of ethylene gas diminished within few minutes and was accompanied by a color change of the reaction mixture from violet to black. In addition, a dark solid residue that was formed, possibly originating from the decomposed catalyst, clearly demonstrated that 110 °C is beyond the thermal stability of this catalyst.

Wagener and co-workers recently described ADMET polymerizations using different classical tungsten systems that are activated and used at higher temperatures (65–120 °C).[28,29] Indeed, our experiments indicated that use of *trans*-dichlorobis(2,6-dibromophenoxy)oxotungsten(VI)/Bu_4Sn (**C3**) allowed increase of the polycondensation temperature up to 120 °C without significant decay of the catalyst during the course of the reaction. Thus, various polymerization conditions were investigated for the $WOCl_2(OAr)_2/Bu_4Sn$ system **C3**. At solvent concentrations below 60% w/w (all solvent concentrations in this work are given as a percentage of the total weight of the reaction mixture), precipitation of the prepolymer **P1** occurred in less than 15 min (see Table 1, **P1.C1**, **P1.C2**, **P1.C3**), which produced materials of only slightly improved $\bar{M}_n$ of around 6000 (see Table 1, **P1.C2**). At a toluene concentration of around 90% w/w, a systematic increase of the polymerization temperature from 97 °C to reflux resulted in delay of the precipitation of **P1** from 1 to 5 h (see Table 1, **P1.C4**, **P1.C5**, **P1.C6**), yielding polymers with a concomitantly increased molecular weight. In the case of **P1.C6**, end group analysis with ^{1}H NMR in fact was no longer possible due to high molecular weight of the polymer. A change of the solvent from toluene to 1,2,4-trichlorobenzene (TCB) at comparable reaction conditions did not lead to further increased polymer molecular weights. To the contrary, a significantly lower degree of polymerization was achieved, indicating that TCB might be a less suitable solvent for the present ADMET reaction (see Table 1, **P1.C7**). Similar results were obtained with *o*-xylene at 105 °C (see Table 1, **P1.C8**), but when elevating the reaction temperature up to 125 °C, number-average molecular weights of up to 8000 were achieved. Unfortunately, analogously to the experiments with **C1** and **C2**, significant fractions of arylvinylic protons were detected in ^{1}H NMR analysis of **P1.C9** and **P1.C10**, which again resulted from the side reactions that took place under reaction conditions close to the thermal limit of the catalyst system **C3**. Further evidence for the thermal application limit of **C3** was obtained with an attempted postcondensation of a polymer **P1** with **C3** at 130 °C. The material obtained under these conditions (see Table 1, **P1.C11**) was found to be insoluble and not meltable, indicative of cross-linking.

Summarizing the results presented above, it is concluded that the optimum reaction conditions investigated here are use of catalyst **C3** in refluxing toluene and at rather dilute concentrations (see Table 1, **P1.C6**) in which polymer **P1** could be kept in solution for approximately 5 h. After the catalytic reduction of **P1.C6** the respective poly(*p*-phenylene butylene) **PPPB.4** had a polydispersity of 3.0 and a HT-GPC $\bar{M}_n$ of 26 000 (see Table 2), which due to the overestimation of the $\bar{M}_n$ by GPC (see below) translates into a more realistic value of $\bar{M}_n$ of the order of 14 000 g mol^{-1}. Our observations seem to suggest that the nature of the solvent, if at all, has only a minor effect on the nature of the polymer produced, while the reaction temperature was found to be the dominating factor. A significant increase in molecular weight was observed when increasing the latter from 97 °C (**P1.C4**) to 110 °C (**P1.C6**). A further increase to 125 or 130 °C seemed to exceed the thermal stability limit of **C3** (**P1.C10** and **P1.C11**). Also WCl_6/Bu_4Sn (**C4**),[30] another classical tungsten system, used at this temperature was unsuccessful, as the resulting polymer (**P1.D1**) was not meltable and insoluble in boiling *o*-xylene.

The above-mentioned occasional production of insoluble materials (**P1.C11**, **P1.D1**) can be explained in view of the emergence of arylvinylic protons (6.15–6.40 ppm) in the ^{1}H NMR spectra of the polymers **P1**, when the respective decomposition temperatures of the catalysts or catalyst systems were approached. At elevated temperatures these arylvinylic functions, caused by undesired side reactions, can readily trigger vinylic polymerization and, hence, yield cross-linked materials.

It is well-known that the olefinic groups of polymers formed by ADMET can be present in either *trans* (*E*) or *cis* (*Z*) form.[23,30,31] The ratio *Z*/*E* of the repeat units in **P1** was determined from ^{1}H NMR spectra (see Figure 3), in which the chemical shift of benzylic protons of a

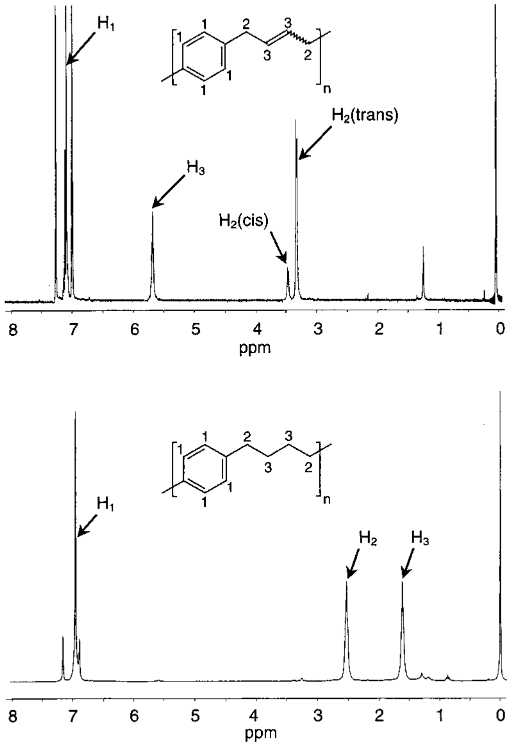


Figure 3. ^1H NMR spectra of precursor polymer **P1.C5** (top) and poly(*p*-phenylene butylene) **PPPB** (produced from **P1.C9**; bottom) measured in 1,2-dichlorobenzene at 80 °C.

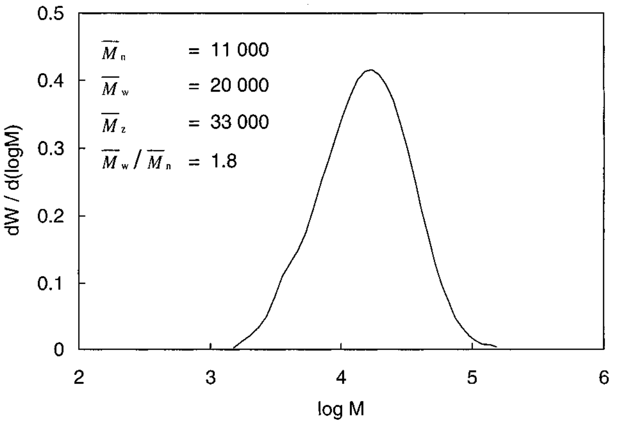
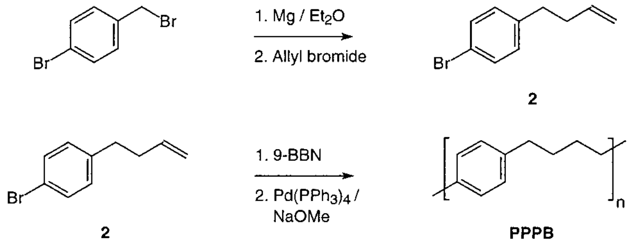


Figure 4. High-temperature gel permeation chromatogram (GPC) of **PPPB.3** (cf. Table 2) measured in 1,2,4-trichlorobenzene at 135 °C.

Scheme 2. Monomer Synthesis and Suzuki Cross-Coupling Polymerization



cis repeat unit (3.43 ppm) differs significantly from the one of the *trans* conformation (3.29 ppm). The assignment of these NMR signals was established by $^1H-^1H$ and $^1H-^{13}C$ correlation spectroscopy (COSY) experiments. The *Z*/*E* ratio of the repeat units in **P1** was found to be independent of the catalyst system and typically around 0.20 (except in materials obtained under conditions that involved a significant amount of side reactions), which is comparable to results obtained by other authors.[30] All relevant reaction parameters for the ADMET polymerizations are compiled in Table 1.

The precursor polymers **P1** were reduced at elevated temperatures (100−125 °C) to yield **PPPB**, employing the catalytic hydrogenation with palladium on activated charcoal as the reduction method (Scheme 1). The reaction conditions of four typical samples and their relevant properties of these materials are collected in Table 2. All polymers were characterized satisfactorily by ^1H and ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), and—in selected cases—elemental analysis. ^1H NMR spectra of polymers **P1** and **PPPB**, recorded in 1,2-dichlorobenzene at 80 °C, are shown in Figure 3. The spectra are consistent with the postulated chemical structure, and it is evident that the olefinic signals (5.64−5.62 ppm) have disappeared virtually fully after reduction.

Polymer Synthesis via Suzuki Cross-Coupling. For the purpose of comparison, **PPPB** was also prepared by the Suzuki cross-coupling of the hydroborated asymmetrical monomer 4-(4′-bromophenyl)-1-butene (**2**), which was synthesized according to Quelet et al.[32] The reaction was carried out in a toluene/THF mixture (2.4/1.0 v/v) using $Pd(PPh_3)_4$ as catalyst and NaOMe as base (Scheme 2). All **PPPB** samples prepared by the Suzuki cross-coupling were also satisfactorily characterized by elemental analysis and NMR spectroscopy. Elemental analysis shows a slight, but systematic, offset from the calculated values, in agreement with the presence of a significant amount of end groups.

Polymer Properties. Molecular Weight Analysis. All polymer samples **P1** and **PPPB** could be dissolved in solvents such as *o*-xylene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and tetralin at elevated temperatures (>80 °C) and, thus, exhibited the desired improved solubility compared to the case of poly(*p*-xylylene), PPX. Molecular weight data were estimated using ^1H NMR end group analysis and high-temperature gel permeation chromatography (HT-GPC) (Figure 4). The molecular weight values of **PPPB** obtained by HT-GPC were systematically higher (by a factor of around 1.8) than those of the prepolymer calculated by ^1H NMR end group analysis. This behavior is consistent and explained by the fact that a polystyrene (PS) calibration was used for the evaluation of the GPC data, which, due the increased rigidity of the **PPPB** backbone when compared to that of PS, leads to a significant overestimation of the molecular weight in HT-GPC. The HT-GPC number-average molecular weights $\bar{M}_n$ obtained for polymers prepared with ADMET polymerization were in the range 4000−26 000 g mol^{-1} (polydispersities typically of between 1.8 and 3), which translates to realistic values of $\bar{M}_n$ of the order of 2500−14 000 g mol^{-1}. Production of higher molecular weights was prevented due to the limited solubility of **P1** and, in particular, the lack of appropriate temperature-resistant ADMET catalysts.

The molecular weights of **PPPB**s prepared by Suzuki cross-coupling were significantly lower than the materials prepared by ADMET polymerization. The maximum number-average molecular weights obtained (determined by end group analysis in the ^1H NMR spectrum) were below 2100 g mol^{-1}, which corresponds to a degree of polymerization of only 16. The low molecular weights of materials obtained with the Suzuki cross-coupling are

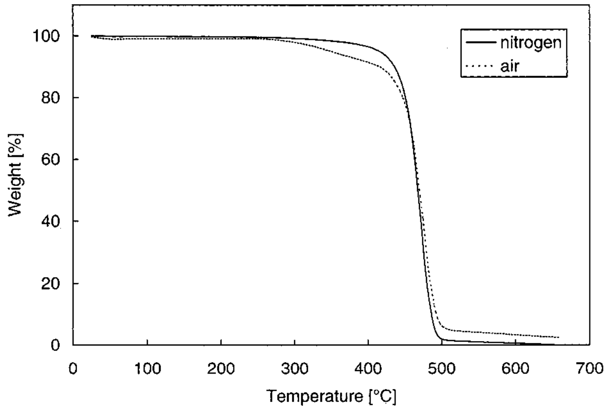


Figure 5. Thermogravimetric analysis of **PPPB** (produced from **P1.C8**) under nitrogen and air (heating rate 20 °C/min).

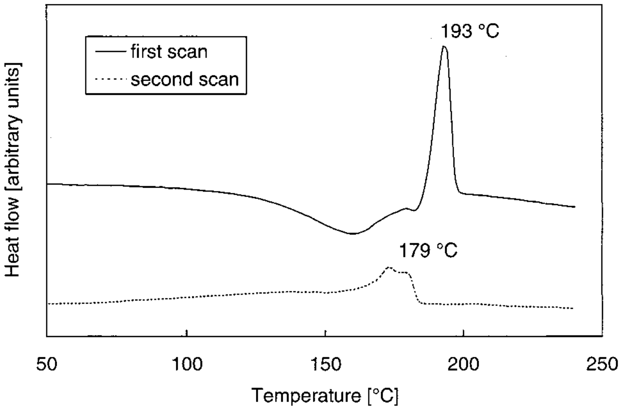


Figure 6. Differential scanning calorimetry of precursor-polymer **P1.C5**.

attributed to the use of the solvent mixture required by the Pd catalyst; the latter is rather unfavorable for the present polymer because it prevents the conduction of the polymerization at temperatures above 100 °C and thus leads to early precipitation of the polymer.

Thermal Properties and Morphology. The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry conducted at heating rates of 10 °C/min. TGA experiments revealed that **PPPB** is remarkably stable under dynamic heating; the new polymer was found to be stable up to around 350 °C under nitrogen atmosphere, as well as in air (Figure 5).

DSC thermograms for the **PPPB**-precursor polymer **P1** (Figure 6) displayed in the first heating scan a broad, exothermic transition with a maximum at around 160 °C. This peak is assigned to the onset of thermal cross-linking of the polymer, clearly evidenced by the fact that unsaturated **P1** heated to 180 °C and kept at this temperature for 10 min is (in contrast to the pristine sample) essentially insoluble in boiling *o*-xylene. This finding is also consistent with the observation that the sharp melt transition at 193 °C of the first heating scan broadened significantly with a maximum at 179 °C in the second heating scan (Figure 6).

DSC scans of **PPPB** revealed a weak transition at around 55 °C, which might be associated with the glass transition T_g and a melting range between 180 and 205 °C (Figure 7a) and 180 and 215 °C (Figure 7b) in the first and second heating scan, respectively. The appearance of two melting peaks could be an indication of the presence of two crystal modifications, as is known for **PPPO**[9] and **PPX**.[6,33,34] After recrystallization of virgin (as-polymerized) **PPPB** at 193 °C, only one pronounced endothermic transition with a maximum at 201 °C was observed (Figure 7c). Recrystallization at 204 °C of preliminarily molten **PPPB** failed to yield material with only one pronounced endotherm in subsequent melting experiments (Figure 7d). Wide-angle X-ray diffraction (WAXD) patterns (Figure 8, middle and right) of all these **PPPB** samples (Figure 7a−d) were found to exhibit the same *d* spacings, which appears to disprove the presumption of the presence of more than one crystal modification. Hence, we attribute the observed effects to phase segregation into crystal domains of significantly different molecular weights, perhaps combined with the presence or absence of extended chain and folded chain crystals, as is well-documented for, e.g., polyethylene in a comparable molecular weight regime.[35] Two melting peaks of **PPPB** may also be due to the melting of two different size crystals (small and large), especially in recrystallized samples.

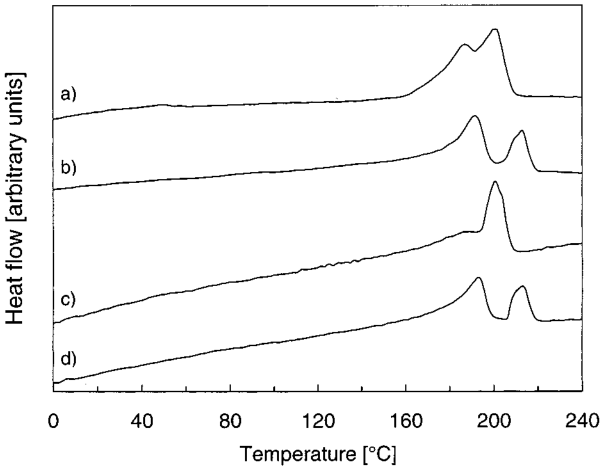


Figure 7. Differential scanning calorimetry of **PPPB** (produced from **P1.C9**): (a) as-polymerized, virgin **PPPB**; (b) **PPPB** crystallized from the melt; (c) as-polymerized **PPPB** recrystallized at 193 °C; (d) DSC scan of once-molten **PPPB**, recrystallized at 204 °C.

Importantly, the melting temperature of **PPPB** is in the attractive range that combines temperature stability and thermoplastic processability and gratifyingly matches the interpolations with our semiempirical approach.[22] It is noteworthy that the **PPPB** produced here has a dramatically different melting behavior than the material that was obtained by Brown and Farthing,[21] for which we do not have a plausible explanation; other than that, these authors may not have produced **PPPB**.

The enthalpy of fusion of **PPPB** was determined to be about 70 J/g, which is indicative of a significant degree of crystallinity of these polymers. This value is comparable to the heat of fusion of commercially available PPX (80 J/g) and to PPX that was obtained by the so-called Gilch route (60−90 J/g).[36,37] The high degree of crystallinity of both the precursor polymer **P1** and **PPPB** was also detected in wide-angle X-ray diffraction experiments. The pattern of **P1** (Figure 8, left) showed a prominent reflection at 4.5 Å and two weaker reflections at *d* spacings of 3.68 and 5.50 Å. The WAXD patterns of virgin **PPPB** that was obtained by pouring a hot, concentrated (around 5% w/w **PPPB**) **PPPB** solution into ethanol displayed ill-resolved reflections resulting from a high degree of disorder (Figure 8, middle). On the other hand, the X-ray photograph of a

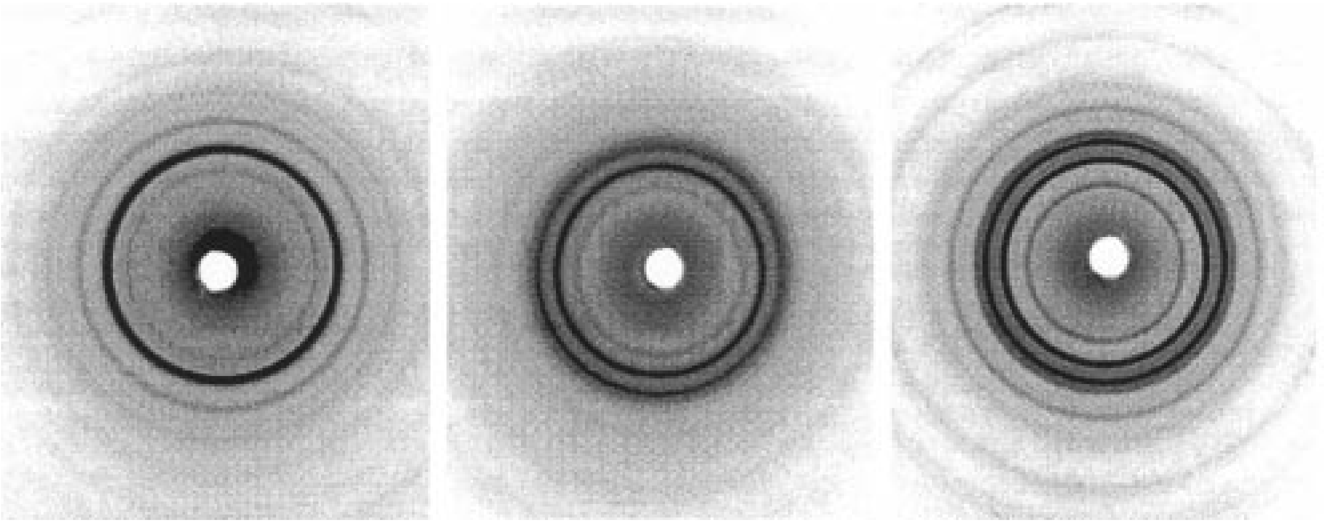


Figure 8. Wide-angle X-ray diffraction patterns of precursor polymer **P1.C4** (left), virgin **PPPB.3** (middle), and **PPPB.3** crystallized from the melt (right).

PPPB sample that was crystallized from the melt exhibited very sharp, well-defined reflections (Figure 8, right). The principal spacings of **PPPB** (Figure 8, right) were 5.09 and 4.36 Å. The respective *d* spacings for the α- (4.0 and 5.2 Å) and β-modification (4.4 Å) of PPX are in a comparable range.[21,38] Additional weak reflections were observed at 3.47 and 6.58 Å. The (weak) diffraction ring corresponding to the largest value, found at 6.58 Å, likely represents the distance between the polymer repeat units, although the value calculated from standard bond lengths and angles[39] (8.37 Å) is higher, which is indicative of tilting of the polymer chains in the crystal unit cell.

Conclusions

We have demonstrated before[9] that acyclic diene metathesis (ADMET) polymerization can be used as an efficient synthetic route to a class of processable, hydrophobic and crystalline polymers that contain only aromatic and aliphatic hydrocarbon units in their backbone. In the present work, poly(*p*-phenylene butylene), as a second member of this class of polymers, was synthesized by the use of four different ADMET catalysts and subsequent, catalytic reduction. Number-average molecular weights of the polymers obtained exceeded 10 000 g mol^{-1}.

Wide-angle X-ray diffraction and DSC experiments showed that both the unsaturated precursor−polymer and poly(*p*-phenylene butylene) displayed a significant degree of crystallinity. In contrast to poly(*p*-phenylene octylene),[9] poly(*p*-phenylene butylene) **PPPB** was found to be soluble only at elevated temperatures and had a high melting temperature in the range from 200 to 215 °C. Thus, **PPPB** indeed exhibits the thermal properties that close the gap between polyethylene and poly(*p*-xylylene).

Elaborate analysis of the crystal structure, mechanical, dielectric, and barrier properties of **PPPB** are in progress and will be published separately.

Experimental Section

General. All reagents and solvents were purchased from Fluka, Aldrich Chemical Co., or Merck. Catalysts **C1** and **C2** were 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 a N_2 atmosphere with water and oxygen concentrations of lower than 1 ppm. DSC and TGA measurements were performed on Netzsch DSC CC 200 and Netzsch TG 209 instruments, respectively. A commercial Parylene N (PPX) film sample (used for the determination of the heat of fusion) was obtained from COMELEC SA, Switzerland. ^1H NMR and ^{13}C NMR spectral data are expressed in ppm relative to internal TMS and were obtained on various Bruker NMR spectrometers. HT-GPC measurements carried out at Montell Polyolefins, Ferrara, Italy, were performed on a Waters 150C ALC/GPC (detector: refractive index; column type: TSK GMHXL-HT, 13 μm; mobile phase flow rate: 0.5 mL/min; solvent: 1,2,4-trichlorobenzene; column temperature: 135 °C; calibration standards: polystyrene). Elemental analyses were carried out by the Microanalysis 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: 12−24 h, 30 mA, 35 kV).

Purification of Monomers, Reagents, and Solvents. Due to the very high sensitivity of some of the ADMET catalysts employed, all chemicals used in conjunction with the ADMET reactions were of utmost purity. Monomer **1** was purified by column chromatography, dried over calcium hydride for 24 h, distilled onto molecular sieve (4 Å), and subsequently deoxygenated by sparging with Ar for at least 2 h prior to use. The absence of water and oxygen in the monomer and the solvents was confirmed by the observation of a persistent purple color, after a sodium/benzophenone indicator solution was added.

Catalyst Synthesis. *trans*-Dichlorobis(2,6-dibromophenoxy)oxotungsten(VI) (C3) was synthesized according to a reported procedure.[40]

Monomer Synthesis. 1,4-Diallylbenzene (1). A 20 mL aliquot of a solution of *p*-dibromobenzene (28.2341 g, 0.1197 mol) in Et_2O (85 mL) was added dropwise to a suspension of magnesium (2.9089 g, 0.1197 mol) in Et_2O (40 mL). After the reaction had started, the remaining aryl bromide solution was carefully added. The resulting mixture was refluxed for 90 min and cooled to room temperature (RT), and allyl bromide (14.969 g, 0.124 mol) in Et_2O (30 mL) was slowly added. After refluxing the reaction mixture for 60 min, it was cooled to RT and dropwise added to a suspension of magnesium (2.8634 g, 0.1178 mol) in Et_2O (30 mL). The resulting solution was refluxed for another 60 min. Another portion of allyl bromide (24.1749 g, 0.1998 mol) in Et_2O (50 mL) was added carefully during a period of 30 min. After stirring at reflux for 80 min, the mixture was poured into ice water (300 mL). The aqueous layer was extracted with ether (3 × 200 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (silicagel 60, hexane) and distillation (bp 40 °C at 0.4 mbar) yielded **1** as a colorless oil (6.0 g, 32%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.12 (s, 4H, Ar), 6.03−5.89 (m, 2H), 5.10−5.02 (m, 4H), 3.36 (d, $J = 6.7$ Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$, 298 K): δ 137.76 (s, 2C, Ar), 137.59 (d, 2C, $CH_2\text{-}\mathit{C}H{=}CH_2$), 128.62 (d, 4C, Ar), 115.62 (t, 2C, $-CH{=}\mathit{C}H_2$), 39.85 (t, 2C, Ar-$\mathit{C}H_2-CH{=}CH_2$). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; Found: C, 91.16; H, 8.71.

4-(4′-Bromophenyl)-1-butene (2).[32] A mixture of 4-bromobenzyl bromide (0.246 g, 0.984 mmol) and Mg (0.479 g, 19.687 mmol) in dry diethyl ether (6 mL) was rapidly heated to reflux, and the exothermic reaction started instantly. The heating was removed, and an additional portion of 4-bromobenzyl bromide (4.675 g, 18.71 mmol) in diethyl ether (14 mL) was slowly added. After the exothermic reaction was finished, the resulting mixture was refluxed for 0.5 h. The greenish solution was allowed to cool to RT, and a solution of allyl bromide (2.382 g, 19.687 mmol) in diethyl ether (2.5 mL) was carefully added. After the exothermic reaction had declined, the reaction mixture was refluxed for another 0.5 h. The upper layer of the phase-separated reaction mixture was subsequently quenched with water (50 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with water (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product (3.23 g, 78%) was purified by distillation; bp 34 °C (0.2 mbar). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.38 (d, $^3J_{(H,H)} = 8.4$ Hz AA′BB′ system, 2H), 7.04 (d, $^3J_{(H,H)} = 8.6$ Hz AA′BB′ system, 2H), 5.88−5.74 (m, 1 H), 5.06−4.94 (m, 2H), 2.68−2.63 (m, 2H), 2.38−2.29 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 140.78 (Ar), 137.60 ($-H\mathit{C}{=}CH_2$), 131.36 (Ar), 130.24 (Ar), 119.58 (Ar), 115.32 ($-CH{=}\mathit{C}H_2$), 35.29, 34.77 (all CH_2). Anal. Calcd for $C_{10}H_{11}Br$: C, 56.90; H, 5.25. Found: C, 56.27; H, 5.18.

Synthesis of Poly(*p*-phenylene but-2-enylene) (P1) by ADMET Polymerization. Solution Polymerization Employing the Schrock Mo Catalyst C1. 1,4-Diallylbenzene (**1**) (0.637 g, 4.025 mmol) was dissolved in toluene (6.20 g). **C1** (5 mg, 6.53 μmol) was added to the rapidly stirred solution. The resulting orange solution started to evolve gas (ethylene). After 60 min, an additional portion of **C1** (4 mg, 5.23 μmol) was added to the orange, opaque reaction mixture. After a total time of 90 min, the temperature was raised to 50 °C. After another 55 min, an additional portion of **C1** (6.5 mg, 8.49 μmol) was added. This procedure was repeated after a total time of 6 h (4.3 mg **C1**, 5.62 μmol) and after 21 h (4.8 mg **C1**, 6.27 μmol) until the evolution of gas ceased. After a total reaction time of 24 h, the pink suspension was precipitated into methanol (50 mL). Polymer **P1.A2** (279 mg, 53%) was obtained as a white, slightly waxy material; mp 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.11 (s, 4H, Ar), 6.40−6.35 (m, traces, arylvinyl), 6.22−6.13 (m, traces, arylvinyl), 6.03−5.89 (m, traces, $-CH_2-C\mathit{H}{=}CH_2$ end groups), 5.70−5.65 (m, 2H, $-C\mathit{H}{=}C\mathit{H}-$), 5.10−5.04 (m, traces, $-CH_2-CH{=}C\mathit{H_2}$ end groups), 3.49−3.47 (m, 0.86H, Ar$-CH_2$-cis), 3.37−3.33 (m, 3.14H, Ar$-CH_2$-trans). ^{13}C NMR (75 MHz, 1,2-dichlorobenzene, 373 K): δ 138.48 (Ar), 130.68 (HC=CH), 128.70 (Ar), 38.75 (CH_2). DP_{NMR}: 14. Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 85.77; H, 8.19.

Solution Polymerization Employing Grubbs Ru Catalyst C2. 1,4-Diallylbenzene (**1**) (1.111 g, 7.021 mmol) was dissolved in toluene (1.15 g) and heated to 111 °C. **C2** (13.2 mg, 16.04 μmol) was added to the rapidly stirred solution, which immediately vigorously evolved gas (ethylene). After 15 min, the evolution of gas had stopped. An additional portion of **C2** (2 mg, 2.43 μmol) was added and, again, initiated the evolution of gas for a short while, indicating the thermal decay of **C2** under these conditions. This procedure was repeated several times, until no significant ethylene production could be observed (total amount of **C2** added: 26 mg). After a total reaction time of 6 h, the reaction mixture was precipitated into ethanol (150 mL). Polymer **P1.B1** (683 mg, 75%) was obtained as a white material; mp 100−145 °C. ^{1}H NMR (200 MHz, 1,2-dichlorobenzene, 353 K): δ 7.12−7.04 (m, 4H, Ar), 6.40−6.33 (m, traces, arylvinyl), 6.26−5.96 (m, traces, arylvinyl and $-CH_2-C\mathit{H}{=}CH_2$ end groups), 5.65−5.54 (m, 2H, $-C\mathit{H}{=}C\mathit{H}-$), 5.13−4.96 (m, traces, $-CH_2-CH{=}C\mathit{H_2}$ end groups), 3.43−3.41 (m, 1.2H, Ar$-CH_2$-cis), 3.29 (s, 2.8H, Ar$-CH_2$-trans). ^{13}C NMR (75 MHz, 1,2-dichlorobenzene, 373 K): δ 138.49 (Ar), 130.70 (HC=CH), 128.72 (Ar), 38.77 (CH_2). DP_{NMR}: 38. Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 90.55; H, 8.57.

Solution Polymerization Employing the Classical Tungsten System C3. 1,4-Diallylbenzene (**1**) (0.636 g, 4.019 mmol) and $WOCl_2(OAr)_2$ (10 mg, 12.9 μmol) were dissolved in toluene (5.02 g) and heated to 85 °C. After 5 min, Bu_4Sn (15 mg, 43.2 μmol) was added to the red solution. After 18 min, the reaction mixture started slowly but acceleratingly to evolve gas (ethylene). Within 1.5 h, the mixture temperature was raised to 111 °C. After 4.5 h a significant amount of precipitated polymer was observed. After a total reaction time of 21 h, the reaction mixture was precipitated into methanol (200 mL). Polymer **P1.C6** (470 mg, 90%) was obtained as a white material; mp 193 °C. ^{1}H NMR (300 MHz, 1,2-dichlorobenzene, 353 K): δ 7.09−7.04 (m, 4H, Ar), 5.64−5.62 (m, 2H, $-C\mathit{H}{=}C\mathit{H}-$), 3.43−3.41 (m, 0.72H, Ar$-CH_2$-cis), 3.29−3.27 (m, 3.28H, Ar$-CH_2$-trans). ^{13}C NMR (75 MHz, 1,2-dichlorobenzene, 373 K): δ 138.48 (Ar), 130.68 (HC=CH), 128.70 (Ar), 38.76 (CH_2). DP_{NMR}: 42. Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.08; H, 8.21.

Solution Polymerization Employing the Classical Tungsten System C4. To a solution of 1,4-diallylbenzene (**1**) (0.777 g, 4.910 mmol) in *o*-xylene (0.780 g) at 130 °C were added a solution of WCl_6 (55.3 mg, 0.139 mmol), Bu_4Sn (89.6 mg, 0.258 mmol), and propyl acetate (48.7 mg, 0.477 mmol) in *o*-xylene (0.709 g). After 5 min, the reaction mixture started slowly to evolve gas (ethylene). After 24 h, an additional amount of *o*-xylene (0.833 g) was added to the dark reaction mixture, and the temperature was raised to 111 °C. After a total reaction time of 52 h, the dark, highly viscous reaction mixture was cooled to room temperature and precipitated into ethanol (150 mL). Polymer **P1.D1** (591 mg, 92%) was obtained as an insoluble, brown-gray material. No melting temperature. T_g at 46−52 °C. Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 85.65; H, 9.00.

Preparation of PPPB by Reduction of Poly(*p*-phenylene but-2-enylene) (P1). Palladium on charcoal (80 mg, 10% Pd) was added to a solution of **P1.C7** (146 mg, 1.12 mmol) in *o*-xylene (60 mL), and the reaction mixture was stirred in a 250 mL glass autoclave at 125 °C for 50 h under a hydrogen pressure of 5 bar. The catalyst was subsequently removed by hot filtration through Celite, and precipitation of the concentrated solution into methanol (120 mL) yielded the white polymer **PPPB.3** (119 mg, 81%); mp 200−225 °C. ^{1}H NMR (300 MHz, 353 K): δ 7.01 (s, 4H, Ar), 2.56−2.53 (m, Ar$-CH_2-$), 1.65−1.60 (m, 4H, Ar$-CH_2-C\mathit{H_2}$). ^{13}C NMR (125 MHz, 1,2-dichlorobenzene, 373 K): δ 139.82 (Ar), 128.43 (Ar), 35.61, 31.19 (all CH_2). Anal. Calcd for $C_{10}H_{12}$: C, 90.58; H, 9.15. Found: C, 89.56; H, 10.15. HT-GPC: $\bar{M}_w = 20\,000$, $\bar{M}_w/\bar{M}_n = 1.8$.

Synthesis of PPPB by Suzuki Cross-Coupling Polymerization. 9-BBN (0.5 M in THF, 11.45 mL, 5.73 mmol) was added to 4-(4′-bromophenyl)-1-butene (**2**) (1.099 g, 5.205 mmol) at 0 °C, and the reaction mixture was allowed to warm to RT within 2 h and subsequently stirred at this temperature for another 5 h. The colorless, clear solution was then added to a suspension of $Pd(PPh_3)_4$ (60.15 mg, 52.05 μmol) and sodium methylate (0.422 g, 7.81 mmol) in toluene (28 mL); the mixture was heated to 60 °C and stirred under reflux. After a total reaction time of 20 h, the reaction mixture was cooled and added dropwise into rapidly stirred methanol (310 mL). After stirring for 1 h, the precipitated polymer was collected and washed with hot ethanol, acetonitrile, and acetone. Drying at room temperature in vacuo overnight yielded **PPPB** as an off-white powder (365 mg, 53%); mp 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.04 (s, 4H), 2.62−2.56 (m, 4H), 1.67−1.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 139.81 (Ar), 128.23 (Ar), 35.36, 31.01 (all CH_2). DP_{NMR}: 14. Anal. Calcd for $C_{14}H_{18}$: C, 90.85; H, 9.15. Found: C, 88.92; H, 9.86.

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