An Improved Synthesis of Poly(*p*-phenylenebutadiynylene)s

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ABSTRACT: A new methodology is described for the synthesis of poly(*p*-phenylenebutadiynylene)s based on the Pd/Cu-catalyzed, benzoquinone-mediated homocoupling of terminal acetylenes. Homopolymers synthesized from the 2,5-dialkoxy-1,4-diethynylbenzene monomers 1,4-bis(decyloxy)-2,5-diethynylbenzene and 1,4-bis(hexadecyloxy)-2,5-diethynylbenzene were largely insoluble, with the soluble portion from the polymerization of 1,4-bis(hexadecyloxy)-2,5-diethynylbenzene exhibiting a number-average molecular weight of 14,000. Completely soluble polymers were obtained from these precursors by the random copolymerization of these monomers. The materials exhibited number-average molecular weights ranging from 67,000 to over 150,000. The ultraviolet–visible and emission spectra of these polymers were examined and found to be very similar to those of structurally analogous poly(*p*-phenyleneethynylene)s and smaller poly(*p*-phenylenebutadiynylene)s reported by Kijima et al. (J Mat Chem, 1998, 8, 2165). © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4669–4676, 2000

Keywords: poly(*p*-phenylenebutadiynylene)s; palladium-catalyzed; homocoupling; benzoquinone; ethynylenes

INTRODUCTION

Over the past 20 years, the design of novel conjugated polymers has constituted one of the major thrusts in the study of electronic materials. Such research is, of necessity, constrained by the availability of suitable methods for preparing polymers with the desired properties. For example, extensive studies of the phase behavior,[1,2] photophysical properties,[3,4] aggregation phenomena,[4–7] and sensory applications[6–9] of poly(*p*-phenyleneethynylene)s have been facilitated by the Sonogashira–Hagihara[8,10,11] and acyclic metathesis reactions,[12,13] which allow for the synthesis of high molecular weight polymers. In contrast, structurally analogous poly(*p*-phenylenebutadiynylene)s have received relatively little attention,[14–20] presumably because of the dearth of appropriate methods for synthesizing these materials. Nonetheless, these polymers are interesting targets, both as conjugated materials and, via their butadiyne linkages, as precursors of thiophenes,[22] pyrroles,[23,24] and poly(diacetylene)s.[25,26]

Butadiynes have been prepared both by copper-mediated homocoupling reactions of terminal acetylenes[27,28] and by cross-coupling methods[29,30] such as the Cadiot–Chodokiewicz reaction of a terminal acetylene with a haloacetylene. Only limited attempts to apply these reaction conditions to the synthesis of poly(*p*-phenylenebutadiynylene)s have been reported, however, and the resulting materials had only low molecular weights [number-average molecular weight (M_n) $\leq$ 11,500].[14–19,21–23] Kijima et al.[18,19] reported an alternative synthesis of short polymers of this type via a palladium-catalyzed reaction in which reductive elimination of two acetylides from a Pd(II) intermediate affords the butadiynyl linkages and Pd(0). This process is made catalytic in palladium with the addition of I_2, which acts as
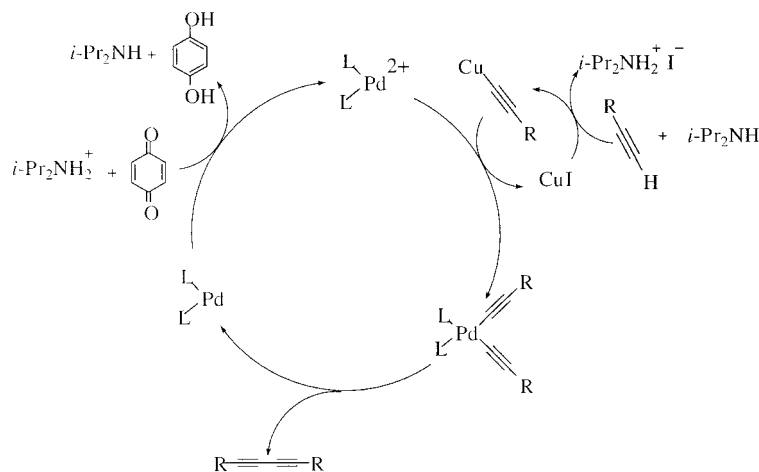
Figure 1. Proposed catalytic cycle for the Pd/Cu-catalyzed homocoupling of terminal acetylenes to form 1,3-butadiynes.

an oxidant to regenerate the active Pd(II) species.[31,32]

Unfortunately, I_2 is known to undergo numerous reactions with terminal acetylenes under reaction conditions that are used for the formation of poly(p-phenylenebutadiynylene)s.[32] Because side reactions lead to chemically inhomogeneous polymers of low molecular weights, it would be highly desirable to employ a mild reagent that is inert toward terminal acetylenes but can rapidly and efficiently convert Pd(0) to P(II). Benzoquinone has been used extensively as a palladium reoxidant in the syntheses of polyketones[33] and indoles,[34] in Wacker-type oxidations,[35,36] and in 1,4-addition reactions of dienes.[37] Therefore, we anticipated that the use of benzoquinone in the catalytic cycle outlined in Figure 1 would provide a means of obtaining poly(p-phenylenebutadiynylene)s with unprecedented molecular weights.
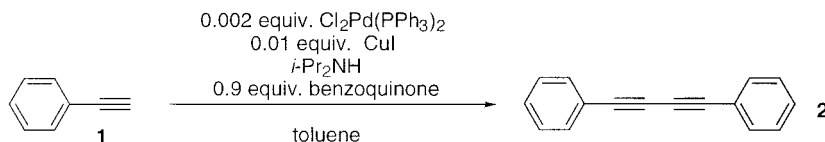
EXPERIMENTAL

Materials

All reagents, unless otherwise noted, were purchased from Aldrich and used without further purification. Aldrich Sure/Seal dimethylformamide (DMF), toluene, and diisopropylamine were used for the reactions; reagent-grade tetrahydrofuran (THF) was dried over sodium, with benzophenone as an indicator. All solvents, including diisopropylamine and triethylamine, were rigorously degassed with argon before use. Benzoquinone was purchased from Aldrich and

recrystallized from ethanol prior to use. Pd-$(PPh_3)_4$, $Cl_2Pd(PPh_3)_2$, and Pd_2dba_3 were purchased from Strem Chemicals, Inc. 2,5-Diethynyl-3-hexylthiophene (**8**) was prepared according to literature procedures[23] from 2,5-dibromo-3-hexylthiophene, which was purchased from Aldrich. The quinones **3** and **4** were prepared according to previously reported procedures,[7] as were the monomers 1,4-bis(decyloxy)-2,5-diethynylbenzene (**5a**) and 1,4-bis(hexadecyloxy)-2,5-diethynylbenzene (**5b**).[8]

General Methods

^{1}H NMR spectra were recorded on a Varian 300-MHz spectrometer, and chemical shifts are reported in parts per million relative to tetramethylsilane (^{1}H spectra) or $CHCl_3$ (^{13}C spectra). The molecular weights of the polymers were determined with a PL gel 5-μm Mixed-C (300 × 7.5 mm) column with both a diode array detector at 254 nm and a refractive index detector at a flow rate of 1.0 mL/min, with THF as the eluent. Molecular weights are reported relative to polystyrene standards purchased from Polysciences, Inc. Spin-cast films were prepared with a Lavall Technologies WS-400-6NPP\Lite spin-coater. Polymer films were cast on a microscope cover glass (18 × 18 mm) at 2000 rpm from 0.5 mg/mL solutions of polymer in chloroform. Mass spectra were determined with a Hewlett Packard 5890 series II gas chromatograph outfitted with a mass selective detector. Fluorescence studies were carried out with a SPEX Fluorolog-τ2 fluorometer (model

0.002 equiv. Cl$_2$Pd(PPh$_3$)$_2$
0.01 equiv. CuI
i-Pr$_2$NH
0.9 equiv. benzoquinone

toluene

1   **2**

Scheme 1

Preparation of 1,4-Diphenyl-1,3-butadiyne (2)

The following procedure is representative of the syntheses described in the text. A mixture of phenylacetylene (**1**; 0.12 g, 1.0 mmol), 1,4-benzoquinone (0.1 g, 0.9 mmol), CuI (0.02 g, 0.01 mmol), and Cl$_2$Pd(PPh$_3$)$_2$ (0.002 g, 0.002 mmol) were combined under Ar in a 25-mL Schlenk tube. Toluene (5 mL) was added to this reaction mixture, followed by 0.2 mL of diisopropylamine. The reaction stirred at room temperature for 3 h under argon and then passed through a short plug of silica, with chloroform as an eluent, to remove inorganic catalysts. An analysis of this mixture by gas chromatography–mass spectrometry (GC–MS) indicated total consumption of the starting material, with only **2** and residual benzoquinone present in the reaction mixture. This mixture was purified by column chromatography on silica gel with hexanes as an eluent to a yield 0.11 g of a white solid (92% yield). ^{1}H NMR (CDCl$_3$), GC–MS, and the melting point of this sample were all in agreement with an authentic sample purchased from Aldrich.

For the purposes of quantifying yields by GC–MS, the aforementioned reaction was carried out in the presence of 0.5 equiv of hexamethylbenzene, which was used as an internal standard. The relative intensities of the GC–MS signals for **2** and this standard were calibrated with standard solutions of known concentrations.

Preparation of Polymers 6c–6f

The following procedure for the preparation of polymer **6c** is representative of all the reactions. **5a** (0.036 g, 0.08 mmol), **5b** (0.050 g, 0.08 mmol), benzoquinone (0.022 g, 0.2 mmol), CuI (0.01 g, 0.05 mmol), and Pd(PPh$_3$)$_4$ (0.005 g, 0.004 mmol) were combined under argon in a sealable Schlenk

tube fitted with a rubber septum. To this were added 3 mL of toluene and 0.5 mL of diisopropylamine. The solution was heated to 60 °C under argon; then, the septum was replaced with a threaded Teflon stopper under a positive pressure of argon. The tube was sealed, and the reaction mixture was stirred at 60 °C for 72 h. The reaction mixture was then cooled, taken up in 50 mL of chloroform, and extracted with a saturated aqueous ammonium chloride solution (3 × 40 mL). The organic phase was then dried (MgSO$_4$), and the solvent was removed under reduced pressure to yield an orange solid. This solid was redissolved in a minimum hot solvent and reprecipitated into methanol. The solid was collected by filtration and washed repeatedly with hot methanol. This solid was then dissolved in chloroform, reprecipitated into acetone, and collected by filtration to yield a bright orange solid (0.073 g, 81% yield). This product was difficult to completely redissolve into chloroform or other organic solvents after it had been precipitated.

Gel permeation chromatography (GPC): M_n = 90,000; weight-average molecular weight (M_w) = 249,000. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.95 (br s, 2H), 3.97 (br t, 4H), 1.81(br m, 4H), 1.2–1.5 (br m, 40 H), 0.86 (br t, 6H). ELEM. ANAL. Calcd. for C$_{36}$H$_{56}$O$_2$: C, 83.10%; H, 10.76%. Found: C, 80.49%; H, 10.73%.

RESULTS AND DISCUSSION

Our preliminary investigations focused on the homocoupling of **1** as a model for the polymerization reaction (Scheme 1). **1** rapidly and quantitatively converted to **2** at room temperature in the presence of excess benzoquinone and catalytic amounts of Cl$_2$Pd(PPh$_3$)$_2$, CuI, and diisopropylamine. Although this reaction was allowed to proceed for 3 h, GC–MS analysis indicated that it was essentially complete after only 45 min.[38] In the absence of benzoquinone, less than 1% of the butadiyne was formed, which can be attributed to coupling affected by the Pd(II) species present at the beginning of the reaction. The omission of any
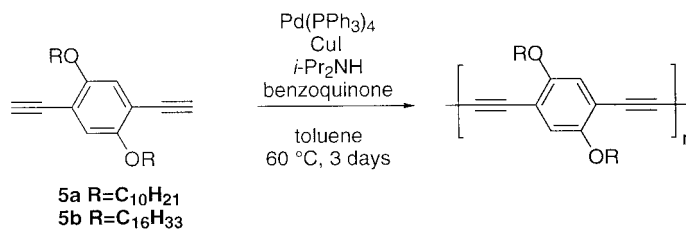
Scheme 2

or all of the catalysts from the reaction mixture resulted in the isolation of only the starting materials. Although the coupling reaction was accompanied by the formal transfer of two protons from the acetylenes to the incipient hydroquinone, no appreciable reaction was observed when it was carried out in the absence of diisopropylamine. This base appeared to act purely as a proton-transfer catalyst because only catalytic amounts of the amine were required for the formation of **2**. In this respect, the homocoupling reaction can be contrasted with the closely related Sonogashira–Hagihara coupling of an acetylene with an aryl iodide, wherein the amine base is required in stoichiometric quantities.

The previously described procedure tolerated considerable variation in the reaction conditions. Thus, the formation of butadiyne proceeded smoothly in a number of solvents, including THF, DMF, and toluene, and in the presence of different bases, such as diisopropylamine and triethylamine. This reaction was also carried out with Pd(0) catalyst precursors such as Pd(PPh$_3$)$_4$ and Pd$_2$dba$_3$, although it was unclear whether these more expensive and less stable catalysts would offer significant advantages over Cl$_2$Pd(PPh$_3$)$_2$. The reaction was also carried out at elevated temperatures (up to 70 °C) to ensure that these conditions would not prove disadvantageous during a polymerization. Consistent with our expectations, no detectable competing reactions or product decomposition arose when the mixtures were heated over periods of up to 4 days.

We also investigated a number of other quinones for their efficacy as oxidants in this reaction. The pentiptycene quinone (**3**) and the triptycene quinone (**4**) both mediated the homocoupling reaction:
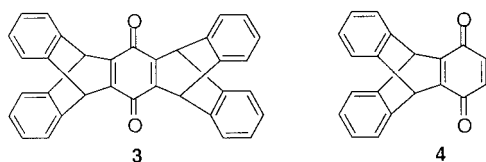

However, these reagents were considerably less reactive than benzoquinone and only worked effectively at elevated temperatures. In contrast, duroquinone, which is a relatively weak oxidant, failed to mediate the formation of butadiynes even after prolonged heating at 60 °C.

Initial efforts to exploit these reaction conditions as a route to poly(p-phenylenebutadiynylene)s focused on the homopolymerization of the diethynyl benzenes **5a** and **5b** (Scheme 2). Intense fluorescence developed immediately after the addition of i-Pr$_2$NH to the reaction mixture, with the emission shifting from violet to green within minutes. Unfortunately, the products obtained after these solutions were heated at 60 °C for 24 h were found, upon workup, to be highly insoluble. GPC analysis of the sparingly soluble fractions obtained from the homopolymerization of **5b** indicated polymers with degrees of polymerization of about 20 (M_n = 14,000).[39] The situation was even more dire for the polymerization of **5a**, which afforded an intractable solid. Even Soxhlet extraction with a variety of solvents failed to yield any soluble polymeric materials from this fluorescent solid. No polymers were produced when the oxidant was omitted from the reaction or in the absence of the palladium, copper, or amine catalysts (as discussed previously).

The formation of insoluble materials during these reactions suggested that high molecular weight polymers were being formed. Nonetheless, it was desirable to demonstrate that soluble (and, hence, analyzable and processable) polymers could be formed via this method. The relative insolubility of higher molecular weight polymers of this type is not surprising; similar solubility problems have been encountered for poly(p-phenyleneethynylene)s containing only hexadecyloxy side chains.[40] In those systems, considerably improved solubilities were found for random copolymers formed from monomers with side chains of different lengths.[40]

A similar approach to solubilizing polymers can conveniently and effectively be applied to the
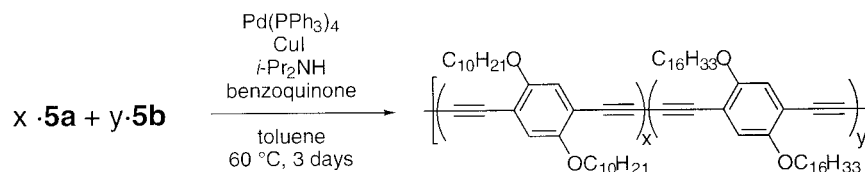
Scheme 3

synthesis of poly(*p*-phenylenebutadiynylene)s by the copolymerization of the monomers **5a** and **5b** (Scheme 3). The reactions of these monomers in various ratios in the presence of 2.5 mol % Pd-(PPh$_3$)$_4$/CuI and excess benzoquinone yielded soluble polymers with molecular weights ranging from 67,000 to 106,000 (Table I).[41] Somewhat surprisingly, the sterically bulky quinone, **3**, also effectively mediated this polymerization, despite its lower reactivity as an oxidant. Indeed, the polymers formed with this reagent were among the largest obtained, with M_n's of up to 154,000 g/mol. In all cases, the reaction mixtures became inhomogeneous during the course of the polymerization reaction, accounting for the high polydispersities obtained. Similarly large polydispersities were also reported by Kijima et al.[18] No end groups were observed in the ^{1}H NMR spectra of these polymers, nor was there any indication from these spectra that benzoquinone was incorporated into the polymer. The ^{1}H NMR spectra for these polymers were in excellent agreement with those previously reported.[18]

Because benzoquinone is consumed stoichiometrically in this reaction, employing substoi-chiometric amounts of this oxidant leads to shorter polymers. Thus, carrying out this polymerization reaction in the presence of 0.95 and 0.90 equiv of benzoquinone gave polymers with molecular weights of 6,400 (**6h**) and 3,800 (**6i**), respectively. In comparison, the theoretically predicted molecular weights for a step-growth polymerization under these limiting conditions are 11,000 and 5,500, respectively.[42,43]

As previously reported, poly(*p*-phenyleneb-utadiynylene)s are, like their poly(*p*-phenylene-ethynylene) analogues, highly fluorescent materials. Figure 2 shows the absorption and emission spectra of polymer **6c** in solution and when cast as a thin film. The spectra of polymers **6c**–**f** are virtually superimposable upon one another; at these high molecular weights, there do not appear to be significant differences in the photophysical properties of the polymers. Moreover, the solution spectra are both qualitatively and quantitatively similar to those reported for smaller molecular weight analogues. As one would expect, however, both the absorption and emission maxima are slightly redshifted in the longer systems. Kijima et al.[18] recently reported the spectroscopic prop-

Table I. Phenylenebutadiynylene Polymers Obtained from Quinone-Mediated Synthesis

Polymer	Monomers	Molar Ratio of the Monomers	Oxidant[a]	Molar Equivalents of the Oxidant[b]	M_n (g/mol)[c]	M_w/M_n[c]
6a	**5a**	N/A	BQ	1.3	N/A[d]	N/A[d]
6b	**5b**	N/A	BQ	1.3	14,000	2.3
6c	**5a + 5b**	1/1	BQ	1.3	90,000	2.8
6d	**5a + 5b**	1/2	BQ	1.3	67,000	2.8
6e	**5a + 5b**	2/1	BQ	1.3	81,000	3.9
6f	**5a + 5b**	2/1	**3**	1.3	154,000	5.2
6g	**5a + 5b**	2/1	BQ	1.1	106,000	3.5
6h	**5a + 5b**	2/1	BQ	0.95	6,400	2.7
6i	**5a + 5b**	2/1	BQ	0.90	3,800	1.9

[a] BQ = benzoquinone.
[b] Relative to the total moles of monomers present.
[c] Determined by GPC analysis versus polystyrene standards.
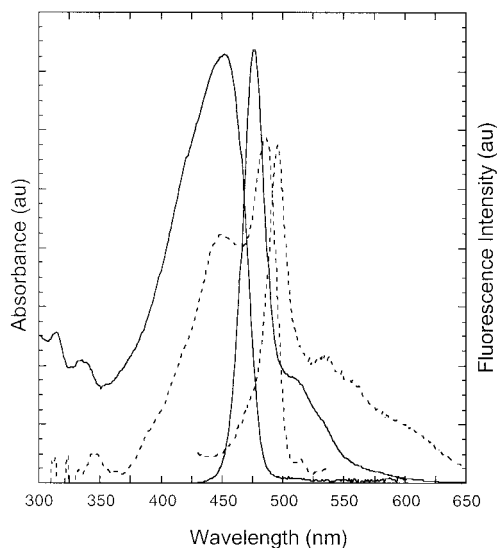[d] Materials obtained were insoluble.

Figure 2. Absorption and emission spectra of polymer **6c** in chloroform (solid lines) and spin-cast films (broken lines).

erties of a short poly(*p*-phenylenebutadiynylene) derived from the polymerization of **5b** (M_n = 5400, M_w/M_n = 2.4). Consistent with its lower molecular weight, Kijima's polymer exhibited absorption and emission maxima (in CHCl$_3$) at 424 and 475 nm, respectively,[18,19] whereas the corresponding values observed for **6c** is at 452 and 477 nm. The emission spectra for both systems exhibit a shoulder at approximately 515 nm. However, in polymer **6c** this peak has a lower relative intensity than in the shorter polymers.

Consistent with earlier reports, the thin-film absorption and emission spectra of **6c–6f** are considerably perturbed from solution. The principle emission is redshifted to 496 nm, whereas the shoulder (which is also shifted) is broader and has a higher intensity relative to the 496-nm peak. The absorption spectrum of **6c**, meanwhile, shows several new peaks at longer wavelengths, including one at 486 nm, which dominates the solid-state absorption. Notably, the broad absorption bands above 500 nm observed by Kijima et al.[18] are absent in the thin-film spectrum of polymer **6c**. In addition, these polymers are much less emissive when cast as thin films than in solution, which suggests, along with the other observations, that there is significant aggregation of the conjugated backbones in the solid state.[6,7]

It is instructive to compare the absorption and emission spectra of **6c** with an analogous poly(*p*-phenyleneethynylene). The spectra of **6c** are very similar to those that have been previously ob-

served for **7**, which has an absorption maximum in CHCl$_3$ at 453 nm and an emission maximum at 478 nm:[7]
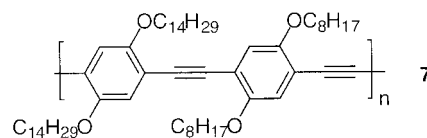

7 also exhibits similar redshifts when it is cast as a thin film; in the solid state, it absorbs at 483 nm and emits at 496 nm. Thus, although diyne linkages are believed to occur to a small extent in the Sonogashira–Hagihara synthesis of poly(*p*-phenyleneethynylene)s,[4] these impurities are unlikely to have a large impact on the photophysical properties of the resultant polymers.

We also attempted to extend our methodology to the polymerization of **8** (Scheme 4). Unfortunately, although the polymers obtained under these reaction conditions were highly soluble, only relatively low molecular weights (M_n = 9500, M_w/M_n = 1.9) were obtained. This result likely reflects the poor stability of **8**, which undergoes fairly rapid decomposition at room temperature.[23]

CONCLUSION

We have demonstrated a new methodology for synthesizing poly(*p*-phenylenebutadiynylene)s based on the Pd(II)/Cu catalyzed homocoupling of terminal acetylenes. The polymers obtained by this method are of considerably higher molecular weights than those obtained by alternative methods such as the Hay coupling. The formation of higher molecular weight materials are also favored in this scheme by the use of benzoquinone as the oxidant, which circumvents the disadvantageous side reactions that are observed when I$_2$ is applied to the palladium-catalyzed homocoupling of terminal acetylenes.
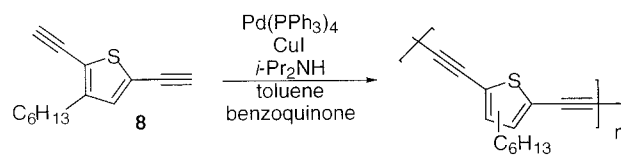
Scheme 4

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38. In all cases reported herein, reactions were carried out under argon to avoid possible reoxidation of the palladium catalyst with O_2. However, control reactions carried out under the same conditions in the presence of oxygen and without benzoquinone led only to very slow, incomplete conversions of **1** to **2**.

39. It is necessary to include a caveat concerning the values of the molecular weights reported herein. At this time, the reliability of the molecular weights of poly(*p*-phenylenebutydiynylene)s, as measured by GPC, versus polystyrene standards is undetermined. By analogy to poly(*p*-phenyleneethynylene)s, however, it is expected that the weights of shorter polymers ($M_n < 50{,}000$) will be systematically overestimated by GPC, whereas the molecular weights of longer, less rigid polymers will be more realistically determined with this method.[44] Moreover, because previous studies of polymers of poly(*p*-phenylenebutydiynylene)s have employed GPC, the method of analysis used herein allows for at least a qualitative comparison of molecular weights.

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41. The polymerization of an equimolar mixture of **5a** and **5b** under Kijima's conditions (i.e., with I_2 as an oxidant) led to molecular weights that were slightly higher than those previously reported ($M_n = 16{,}000$ g/mol, $M_w = 36{,}300$ g/mol). These lower molecular weights were, nonetheless, still considerably lower than those obtained when benzoquinone was employed as an oxidant.

42. The number-average degree of polymerization (DP) for a step-growth polymerization is equal to 1/(1

$- p$), where p is the extent of the reaction. For reactions that proceed to 95 and 90% completion, this corresponds to DP = 20 and 10, respectively. See Elias, H. G. An Introduction to Polymer Science; VCH: Weinheim, 1997.

43. The disparity between the predicted and observed values were accounted for by the errors associated with the use of GPC for determining the molecular weights of short, rigid-rod polymers of this type (see refs. 39 and 44). Some errors might also have arisen, however, from an incomplete reaction of benzoquinone with palladium, which would lead to lower molecular weight materials. In all other cases, benzoquinone was used in sufficient excess so that this would not be a limitation on the molecular weight obtained.

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