High Molecular Weight Poly(*p*-phenyleneethynylene)s by Alkyne Metathesis Utilizing "Instant" Catalysts: A Synthetic Study

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ABSTRACT: In this contribution, alkyne metathesis of 1,4-dipropynylated benzenes **3** is reported. High-molecular weight poly(*p*-phenyleneethynylenes) **4** form from **3** under concomitant evolution of butyne. The highly active catalyst system employed in this polymerization reaction forms from commercially available $Mo(CO)_6$ and 4-chlorophenol or 4-trifluoromethylphenol in situ at 140 °C in off-the-shelf quality 1,2-dichlorobenzene. Introduction of dry nitrogen into the reaction vessel serves to remove the byproduct, 2-butyne. Several dipropynylated benzenes **3** carrying solubilizing alkyl (hexyl, nonyl, dodecyl, 2-(ethyl)-hexyl, ethylbutyl, isopentyl, 3,7-dimethyloctyl, 2,5,5-trimethylhexyl, cyclohexyl, isopentyloxy) or alkoxy substituents were prepared starting from 1,4-dichlorobenzene (alkyl substituted) or hydroquinone (alkoxy substituted). Polymerization of the monomers **3** furnished the yellow and highly fluorescent poly(*p*-phenyleneethynylene)s **4** in excellent to quantitative yields and high purity. For soluble derivatives, the degree of polymerization (P_n) is observed in the range $1 \times 10^2 \leq P_n \leq 13 \times 10^2$, while the polydispersities (M_w/M_n) appear in a bracket, $2 \leq M_w/M_n \leq 4.5$. Miscellaneous optimizations (time, temperature) were performed. Maximum molecular weights are obtained at reaction temperatures around 130−150 °C and reaction times of 25−30 h.

Introduction

The formation of C−C multiple bonds is a fundamental topic and challenge in organic, organometallic, and polymer chemistry. Many different routes including elimination, substitution, rearrangement, and condensation have been developed toward this end.[1] For the construction of alkenes, the process of alkene metathesis in all of its variants (ring opening, ring closing, acyclic) has become a well-established and powerful instrument in the tool kit of the synthetic organic chemist.[2] By now olefin metathesis can be considered a legitimate and potent competitor to the more established methods of C−C double bond formation such as the McMurry coupling[3] or the Wittig reaction.[4] Compared to that, the chemistry of the C−C-triple bond has been dominated almost exclusively by the—admittedly extremely effective—Pd-catalyzed couplings of the Stille or Heck−Cassar−Sonogashira−Hagihara type[5]—which renders the preformed alkyne unit as a module to the unsaturated core under consideration. A synthetically useful analogue of the Wittig or McMurry reaction is unknown in the chemistry of the C−C triple bond, despite the fact that the direct transformation of aldehydes into alkynes has been accomplished successfully.[6]

On the other hand, alkyne reformation (i.e. the scrambling of substituents in internal alkynes) has been known for over 25 years. Yet it has never found the attention its cousin, alkene metathesis, has received so lavishly.[7] Only very recently has alkyne metathesis been "discovered" as an attractive synthetic tool.[8] The first reported example was the preparation of polyooctynamer through ring-opening of cyclooctyne by (tBuO)$_3$W≡C-tBu.[9] Later Bazan[10] reported the ring opening of tetrasilacyclooctadiynes by a molybdenum carbyne complex, which afforded novel silicon-containing conjugated polymers. The breakthrough for the use of the tungsten carbyne complex (tBuO)$_3$W≡C-tBu with regard to synthetic applications is the recent discovery, by Weiss[11a] and Fürstner,[11b] that ring-closing alkyne metathesis of dipropynylated substrates can be performed. On the other hand, Mori showed, in 1995, that the Mortreux catalyst system,[12] a mixture of $Mo(CO)_6$ and 4-chlorophenol, is useful to couple internal alkynes, although the reported yields were often moderate and never exceeded 80%. Yields in this range are not sufficient to access high molecular weight polymers, which made these catalysts unattractive by appearance for the polymer community.

We have a long standing engagement in the synthesis of alkyne-bridged oligomers and polymers.[13] Specifically, we were interested in finding a route to high molecular weight poly(*p*-phenyleneethynylene)s (PPEs, **4**). We and others have discussed in depth why the highly fluorescent PPEs are attractive materials for optical and electronic applications.[14] This contribution is limited to preparative−synthetic aspects of PPE formation under the condition of alkyne metathesis.

The classic method to make PPEs **4** and related poly(aryleneethynylene)s is the Pd/Cu-catalyzed coupling of dihalogenated (Br, I) arenes or benzenes to diethynylated aromatics in an amine as solvent.[5,14,15] This represents an (AA + BB) type polycondensation. Alternatively, an AB monomer carrying both a free alkyne group and an iodide function can be used in this polycondensation to avoid problems arising from imbalanced stoichiometries.[14a] However, these Pd-catalyzed couplings have several distinct disadvantages:

- The obtained degrees of polymerization (P_n) almost never exceed $P_n < 50-80$ and are more in the region of $P_n \approx 20-40$, unless an acceptor-substituted dihaloarene is used.[14h,p,16]
- Some percentage of butadiyne defects is always produced due to homocoupling of the used alkyne

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monomer. This homocoupling reaction is promoted by the presence of trace amounts of oxygen in the reaction mixture and due to the necessary reduction of the palladium(II) catalyst precursors.

•The end groups in these polymers are somewhat ambiguous due to dehalogenation or conversion of some of the iodinated sites into triphenylphosphonium groups.[17]

•An additional problem is the use of large amounts of amine as solvent and the concomitant production of ammonium salts, which both are undesirable from an ecological point of view.

•Last but not least, the complete removal of palladium- and phosphorus-containing catalyst residues is not always facile.

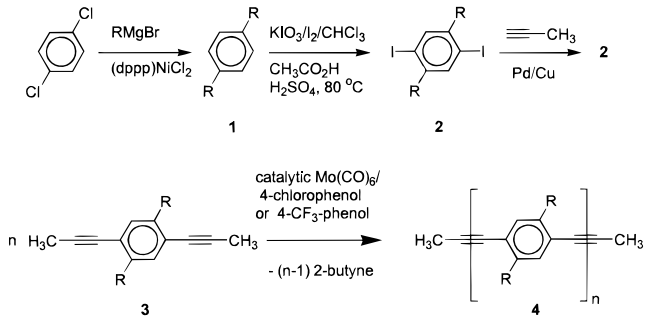
These shortcomings of the popular Pd-catalyzed condensation[17] led us to explore alkyne metathesis as an attractive alternative. The superbly active but not commercially available Schrock tungsten carbyne (tBuO)$_3$W≡C-tBu was used in our first metathesis experiments. The complex is sensitive toward water and air, so that all of the polymerizations had to be conducted in rigorously dried and degassed solvents.[18] The obtained PPEs showed $P_n \leq 100$, clearly demonstrating that alkyne metathesis is competitive to the best reported Pd systems.

The use of the archaic Mortreux catalyst system, made by mixing $Mo(CO)_6$ and a suitable phenol in off-the-shelf, nondried solvents, however, would be extremely attractive when compared to the use of preformed Schrock carbyne complexes. This would be true for applications both in an academic setting as well as for industrial scale-up if the intrinsic limitations with regard to the unsatisfying metathesis yields could be overcome. *We have been able to do that.* Modification of the reaction conditions now allow one to perform acyclic diyne metathesis (ADIMET) of 1,4-dipropynylated benzenes **3** under formation of high molecular weight PPEs **4**.[19]

A full, expanded, and detailed synthetic account of the ADIMET synthesis of PPEs **4** utilizing a mixture of $Mo(CO)_6$ and 4-chlorophenol or 4-trifluoromethylphenol as catalyst systems is presented here.[19] Materials properties (phase behavior, fluorescence, aggregation) of the obtained PPEs are currently under intense investigation in our laboratories and are discussed elsewhere.[20]

Results

Synthesis of the Precursors. For a successful preparation of PPEs **4** via ADIMET, the corresponding 1,4-dipropynyls **3** have to be accessible in large quantities and good yields. While **3a** was already known and described in the literature,[8,14a] synthetic procedures for the other derivatives of **3** are provided. Kumada coupling[21] of 1,4-dichlorobenzene with 2 equiv of an alkyl Grignard reagent in diethyl ether gives rise to the formation of the corresponding dialkylated benzenes **1b**−**j**, which were iodinated after distillation without further characterization. Iodination of dialkylated benzenes is well-described. A mixture of KIO_4 or $H_2I_2O_7$ in acetic acid, sulfuric acid, and chloroform transforms **1b**−**j** into the iodides **2b**−**j** in fair to excellent yields.[22] In some cases we had to prolong the reaction time from 18 to 48 or 72 h. A small aliquot was removed, worked up, and checked by NMR. If the reaction was complete, only a singlet at δ 7.8 was observed in the aromatic region while the signal at δ 6.9 had disappeared. Diiodides **2a,i** were already described in the literature.[14,22] Efficient propynylation of **2a**−**j** in a Heck−Cassar−Sonogashira−Hagihara reaction was performed in a closed system under an atmosphere of propyne to ensure its economical use. Of the gaseous alkyne, 2.1−2.2 equiv were applied per equivalent of diiodide. Piperidine or piperidine/THF mixtures were the most effective,[23] and vigorous shaking of the reaction flask enhanced the uptake of the alkyne. Aqueous workup and crystallization from ethanol combined with column chromatography furnished **3a**−**j** in good to excellent yields.



*Substituent Key for **1** - **4***

a Hexyl; **b** nonyl; **c** dodecyl; **d** isopentyl; **e** ethylbutyl; **f** ethylhexyl; **g** 2,5,5-trimethylhexyl; **h** 3,7-dimethyloctyl; **i** isopentyloxy; **j** cyclohexyl

The Hexyl Polymer 4a, a Preliminary Case Study. From our prior experience with PPEs, we knew the physical and spectroscopic properties of **4a** well;[8,14a] therefore **3a** was used to optimize the metathesis conditions. In the first experiment (Table 1, entry 1) we treated **3a** in 1,2-dichlorobenzene at 110 °C for 16 h with a mixture of $Mo(CO)_6$ (5 mol %) and 4-(trifluoromethyl)-phenol (100 mol %). Workup provided a 60% yield of light yellow **4a** with a P_n of 19. To ensure complete removal of butyne, in the subsequent experiments, a slow stream of N_2 was passed over the reaction mixture. To accelerate the reaction rate, we simultaneously increased the reaction temperature to 150 °C under otherwise identical conditions (entry 2). *A quantitative yield of **4a** (yellow flakes) was obtained.* Gel permeation chromatography (GPC) indicated a P_n of 73, and the polydispersity M_w/M_n was determined to be 3.8. This batch of **4a** was only sparingly soluble in chloroform or dichloromethane, and NMR spectroscopic characterization had to be performed at elevated temperature in tetrachloroethane-d_2. When the reaction temperature was further raised to 180 °C, a higher molecular weight polymer was obtained with a P_n of 1.8×10^2 and a polydispersity of 5.4. This batch of **4a** was brownish, not bright yellow, and was less soluble in chloroform (entry 3). Its ^{13}C NMR spectrum, however, indicated the formation of PPE without structural defects. In a second set of experiments (entries 4−6) we used the much cheaper 4-chlorophenol as the phenolic activator and observed a similar trend. At 120 °C only low-molecular weight **4a** (P_n = 22, determined by ^{1}H NMR; P_n = 41 by GPC) formed, but at 130−150 °C, we obtained PPEs in almost quantitative yield (see Table 1) with P_n values of 1.0×10^2 and 1.5×10^2, respectively. The determination of molecular weights via ^{1}H NMR spectroscopy was performed by integration of the residual propyne methyl groups (six hydrogens) at δ 2.1 vs the integral of the methylene groups (four hydrogens) at δ 2.5. This approach only works for $P_n < 100$ (integral ratio 33:1).

Table 1

entry	substituent[k]	amt of monomer **3**, g (mmol)	temp, °C	yield PPE **4**, g	P_n(GPC)	M_w/M_n
1[b]	**a**	0.500 (1.55)	110	0.251 (60%)	19	1.8
2[b]	**a**	0.500 (1.55)	150	0.440 (>99%)	73	3.8
3[b]	**a**	0.500 (1.55)	180	0.402 (96%)	182	5.4
4[a]	**a**	0.500 (1.55)	120	0.350 (84%)	41	2.5
5[a]	**a**	1.00 (3.10)	130	0.900 (>99%)	97	5.0
6[a]	**a**	2.50 (7.76)	150	2.23 (>99%)	146	5.0
7[c]	**a**	0.500 (1.55)	150	0.404 (96%)	222	6.7
8[a]	**b**	5.00 (12.3)	150	4.55 (>99%)	189	3.1
9[a]	**c**	0.500 (1.02)	150	0.411 (92%)	639	6.9
10[b]	**c**	0.500 (1.02)	150	0.550 (>99%)	354	4.5
11[a,e]	**c**	0.500 (1.02)	150	0.433 (97%)	197	3.9
12[a]	**d**	2.00 (6.79)	150	1.76 (>99%)	35 sf[d]	2.6
13[b]	**d**	1.38 (4.69)	150	1.02 (91%)	16 sf[d]	3.3
14[b]	**e**	0.500 (1.55)	150	0.400 (96%)	25 sf[d]	3.5
15[b]	**f**	1.000 (2.64)	150	0.946 (>99%)	172	3.8
16[b]	**f**	0.500 (1.32)	110	0.401 (93%)	29	2.2
17[b]	**f**	1.00 (2.64)	175	0.760 (89%)	1260	3.5
18[b,f]	**f**	0.500 (1.32)	150	...	...	...
19[b,g]	**f**	0.100 (0.264)	150	0.091 (>99%)	291	6.9
20[a]	**f**	2.00 (5.28)	150	1.38 (80%)	21	1.8
21[a]	**g**	1.50 (3.69)	150	0.906 (70%)	43	2.2
22[a]	**g**	5.00 (12.3)	150	4.508 (>99%)	23	1.8
23[a,h]	**g**	1.50 (3.69)	150	0.987 (76%)	13	1.5
24[a,i]	**g**	1.50 (3.69)	150	1.240 (95%)	47	2.5
25[b]	**h**	0.873 (2.01)	150	0.771 (>99%)	20	4.0
26[a]	**i**	1.02 (3.11)	130	0.251 (29%)	8	1.5
27[b,i,j]	**i**	0.500 (1.52)	130	0.443 (>99%)	65	2.5
28[b]	**i**	0.500 (1.52)	170	0.100 (24%)	21	2.2
29[a]	**j**	0.250 (0.785)	150	0.209 (>99%)	10 sf[d]	1.3
30[b]	**k**	0.516 (1.601)	150	0.540 (>99%)	265	5.6
	hexyl					
	isopentyl	0.118 (0.401)				
31[a]	**l**	1.64 (5.09)	150	3.27 (91%)	87	3.7
	hexyl					
	dodecyl	2.50 (5.09)				
32[b]	**h**	0.517 (1.19)	130	0.442 (97%)	286	5.3

[a] *p*-Chlorophenol. [b] *p*-Trifluorocresol. [c] Bis(trifluoro)cresol. [d] sf: soluble fraction. [e] 12% catalyst. [f] Neat. [g] Double polymerization. [h] Heat catalyst to 150 °C, and then add monomer. [i] Heat catalyst to 80 °C, and then add monomer. [j] 10% catalyst. [k] Substituent key: **a**, hexyl; **b**, nonyl; **c**, dodecyl; **d**, isopentyl; **e**, ethylbutyl; **f**, 2-(ethyl)hexyl, **g**, 2,5,5-trimethylhexyl; **h**, 3,7-dimethyloctyl; **i**, isopentyloxy; **j**, cyclohexyl.

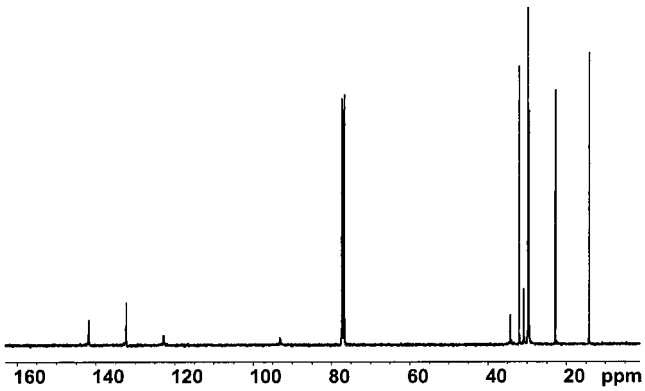


Figure 1. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

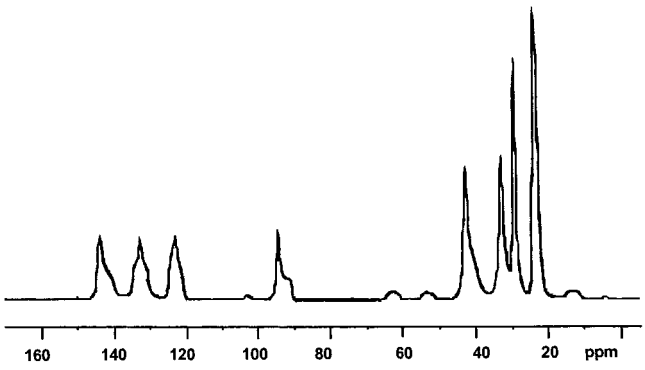


Figure 2. Solid-state CPMAS ^{13}C NMR spectrum of **4d**. Signals: 120−150 ppm, aromatic core; 94.3 ppm, alkyne groups; 42.7 ppm, benzylic carbons; 32.9, 29.3 ppm, CH_2CH_2 fragment; 23.8 ppm, methyl groups. The other small signals observed at 15, 52, 62, and 100 ppm are spinning sidebands, while the shoulder in the signal of the alkyne carbon and the aromatic carbons are artifacts.

Above that ratio, integration is not reliable anymore, and in the case of the high molecular PPEs, the signal for the propyne group is absent. The polydispersities in these polymers are around 5.0. Changing the phenolic activator to the more acidic 3,5-bis(trifluoromethyl)-phenol (entry 7) at a reaction temperature of 150 °C, raised P_n to 2.0×10^2. In this case, however, the polydispersity is high ($M_w/M_n = 6.7$). According to ^{13}C NMR spectroscopy **all** of the obtained PPEs **4** are defect free (Figures 1−3, vide infra). How can the high observed polydispersities be explained? An ideal step−growth polycondensation would lead to a Flory−Schulz distribution of the molecular weights of our PPEs **4** with $M_w/M_n = 2$. However, this would apply only to our case if the propynyl groups in the monomer **3** were of a reactivity identical to that of the terminal, reacting propynyl groups in the growing polymer chain **4**. This condition, however, is probably not given. In conjugated polymers such as **4**, the HOMO and LUMO are in an obvious way dependent upon P_n. Both the HOMO and LUMO will strongly affect the reactivity of the active propyne end group in the forming polymer chain. As a consequence, deviation from the ideal Flory−Schulz distribution (i.e., increased polydispersities in **4**) is not too surprising.

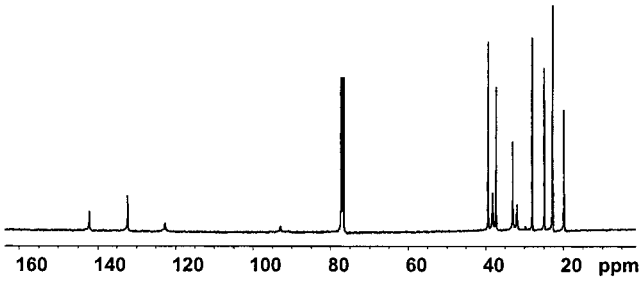


Figure 3. ^{13}C NMR spectrum of **4h** in $CDCl_3$.

Branched Substituents. The optimization performed for the synthesis of **4a** allowed examination of the ADIMET reaction of other dipropynyls. We were surprised to find that both **3d** (isopentyl) and **3e** (ethylbutyl) gave insoluble yellow polymers in high yield (Table 1, entries 12−14). They were characterized by solid-state NMR and elemental analysis. Their soluble fractions were examined by UV−vis spectroscopy and GPC. All of the collected data support the formation of PPEs **4d** and **4e**. The solid-state NMR of **4d** is displayed in Figure 2 and exhibits the expected number of signals. The alkyne carbons show one resonance at δ 94.3.

A considerably increased solubility of PPEs **4** was found when subjecting **3g** (3,5,5-trimethylhexyl) or **3f** (2-ethylhexyl) to the conditions of alkyne metathesis. In the case of **4g**, P_n is low and varies from 13 to 47 (GPC). Entries 21 and 22 are good examples of the difficulties of molecular weight control in **4g**: utilizing the same reaction conditions in two independent experiments renders different numbers of repeating units (P_n = 43 and 23, respectively). Heating the catalyst system in 1,2-dichlorobenzene to 150 or 80 °C in two parallel experiments prior to the addition of the monomer has no influence on the number of repeating units or the polydispersity (entries 23 and 24) in **4g**.

The molecular weight of the 2-(ethyl)hexyl-substituted PPEs **4f** grows with increasing temperature from a P_n of 29 at 110 °C to 1.7×10^2 at 150 °C and finally to a surprising 1.3×10^3 at 175 °C with a polydispersity of M_w/M_n of 3.5 (Table 1, entries 15−17). Accordingly, the latter shows less but still sufficient solubility in chloroform. Despite the high polymerization temperature, however, ^{13}C NMR spectroscopy shows the absence of defects. The use of 4-chlorophenol at 150 °C is less effective for the production of **4f** and leads only to low molecular weight PPE (entry 20). In a "double polymerization experiment", the ethylhexyl polymer **4f** (entry 15) was subjected to the polymerization conditions a second time, which increased P_n from 1.7×10^2 to 2.9×10^2 (entry 19). Solventless processes are of interest in industrial applications, polymerizing monomers directly into casts. However, an ADIMET experiment performed upon **3f** without solvent under otherwise unchanged reaction conditions (entry 18) only leaves black decomposition products behind, while no productive polymerization occurs.

To access hitherto unknown, optically active PPEs,[14b] a monomer carrying two chiral side groups (**3h**) was prepared by the standard route and its ADIMET was investigated. A high molecular weight PPE **4h** formed at l30 °C with trifluorocresol as phenolic activator. This polymer did not display any end group signals in its ^1H NMR spectrum (entry 32). GPC of **4h** showed a P_n of 2.9×10^2. In a parallel experiment at 150 °C, P_n reached a value of ≈20, which indicates a certain difficulty of molecular weight control. The ^{13}C NMR spectrum of **4h** is shown in Figure 3 and discussed: In the aromatic region, three signals are observed as expected for a 1,4,2,5-tetrasubstituted benzene ring. One alkyne resonance is recorded at δ 93.0, and the nine signals visible in the aliphatic region can be assigned to the solubilizing alkyl groups. Interestingly, the two stereo centers in the repeating unit of **4h** are separated too far for diastereotopic splitting of any spectral lines to be observed. No additional signals are visible in the aromatic or the vinylic region, excluding cross-linking by alkyne trimerization or polymerization. These findings support the formation of a defect-free PPE chain. Of course, due to the intrinsic limits of the method, structural defects which occur in ≪5% of the repeating units are "invisible" by NMR spectroscopy.

As expected, the polymerization of a cyclohexyl-substituted **3j** only yields oligomeric material. GPC of the soluble fraction of **4j** indicates a P_n of 10 with a narrow polydispersity of 1.3 (entry 29). Additionally, two copolymerization experiments were undertaken. A combination of 80% hexyl (**3a**) and 20% isopentyl (**3d**) monomers was polymerized under standard conditions (4-chlorophenol, 150 °C), furnishing a high molecular weight PPE in excellent yield. GPC indicated a P_n of 2.7×10^2 (entry 30). However, if a combination of 50% hexyl and 50% dodecyl monomers at the same temperature but with 4-(trifluoromethyl)phenol as phenolic activator is utilized, a polymer with lower molecular weight was produced with a P_n value of 0.9×10^2 (entry 31). The observed polydispersities are in the bracket 3.7−5.6.

High Molecular Weight PPEs. To examine other monomers, nonyl-substituted **3b** was polymerized, which gave **4b** in quantitative yield and a P_n of 1.9×10^2. The polymer **4b** is of considerably higher molecular weight than **4a** (Table 1, entry 8). Side chain elongation with enhanced solubility of **4** seemed to lead to an increase in P_n. With that regard, dodecyl substituents should be an even better choice for the synthesis of high molecular weight PPEs. Indeed, several runs (Table 1, entries 9−11) showed that P_n can reach values between 2 and 6.4×10^2 for **4c**. The latter value is remarkable for a PPE made by a step−growth process. The observed high molecular weight must be a consequence of the excellent solubilizing properties of the dodecyl groups and the remarkable activity of the "instant" catalyst system. However, not every run gives these high molecular weights, but P_n values above 2×10^2 are always reached. Out of five experiments with the dodecyl monomer (**3c**), four showed P_n values above 5×10^2. A ^{13}C NMR of a representative example (**4b**) is shown in Figure 1.

Miscellaneous Optimizations. An important parameter is the dependence of the molecular weight of **4** with regard to the reaction time. To clarify this point we investigated the time dependence of P_n and M_w/M_n in both **4c** and **4f**. Samples were drawn after defined time intervals and the aliquots examined by GPC. Figure 4a shows four graphs in which the dependence of P_n is plotted vs the polymerization time (experiment 1 (**3c**), diamonds; experiment 2 (**3c**), circles; experiment 3 (**3f**), squares; experiment 4 (**3f**), triangles). In all of the experiments, the maximum P_n seems to be reached after approximately 30 h of reaction. The P_n vs time curve is roughly sigmoidal, as is expected for a step−

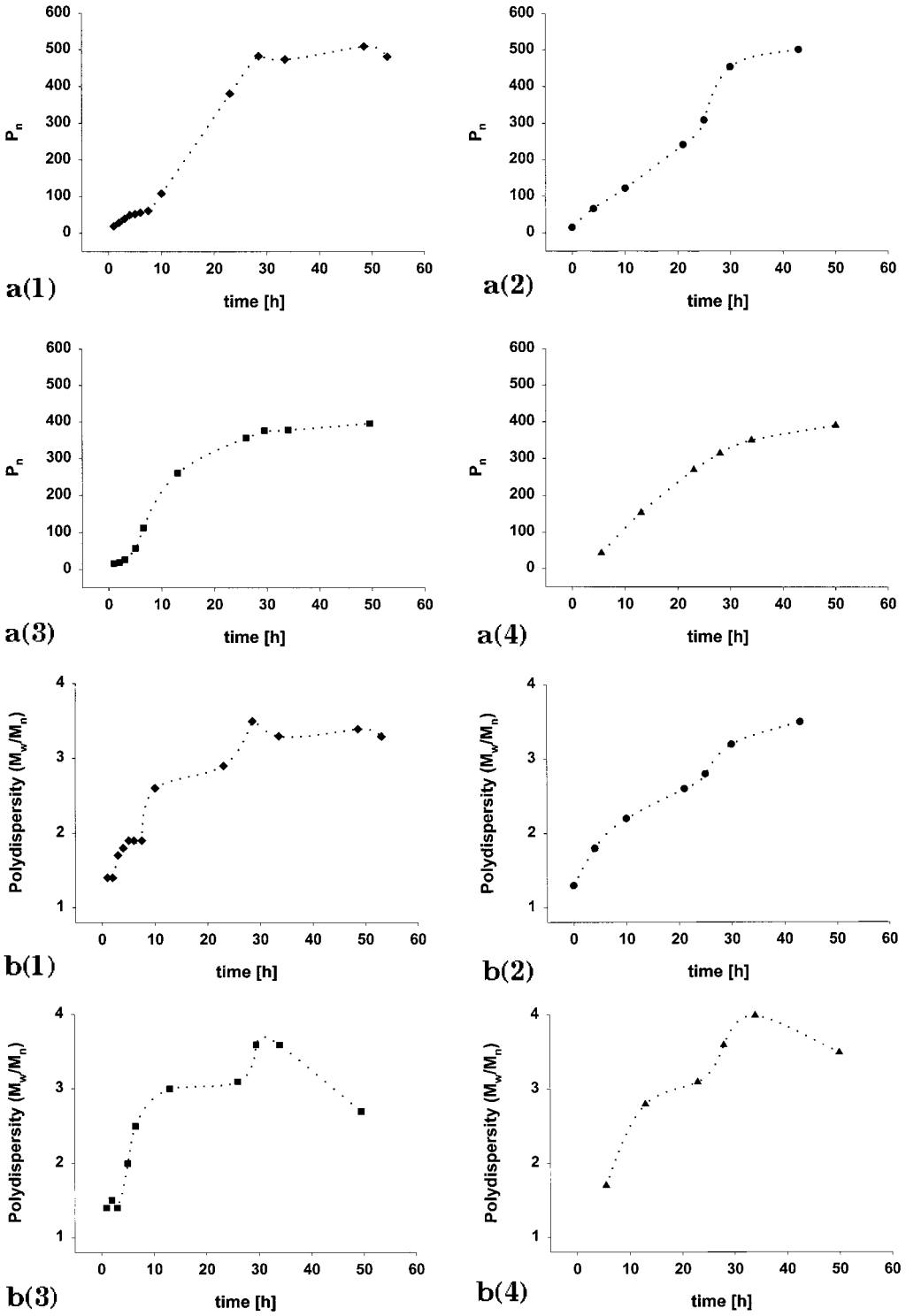


Figure 4. (a) Time experiments: Degree of Polymerization P_n vs reaction time. Key: experiment 1, diamonds, formation of **4c**; experiment 2, circles, formation of **4c**; experiment 3, squares, formation of **4f**; experiment 4, triangles, formation of **4f**. (b) Time experiments (development of polydispersity (M_w/Mn) vs reaction time): experiment 1, diamonds, formation of **4c**; experiment 2, circles, formation of **4c**; experiment 3, squares, formation of **4f**; experiment 4, triangles formation of **4f**.

growth process; at the beginning, P_n increases only slowly, until all monomer and small oligomers are consumed. This is followed by a period of fast growth of P_n. However, once the viscosity of the reaction mixture is high and the reacting propynyl groups are depleted, the molecular weight increases only marginally or not at all. In the herein examined cases, the polydispersity (M_w/M_n) of the formed polymer is low in the beginning (1.4−1.6) but reaches a value of 3−4 after 30 h of reaction (Figure 4b). However, the elution peaks in the GPC indicate a monomodal distribution of the molecular weight, excluding cross-linking under network formation. Figure 4a shows that considerable control over P_n can be exerted by correct selection of the reaction time. It is possible to make low molecular weight polymers by this method, if the reaction is run for only 2 or 3 h.

The second parameter to be looked at is the content of the phenolic activator chlorophenol in these experi-

ments. While 4-chlorophenol (**5**) is cheap, it is not environmentally friendly. We typically use 1 equiv of **5** per reacted monomer **3** or 20 equiv per used $Mo(CO)_6$. This is not a problem in an academic setting but will be of concern for an industrial application of this process. Therefore, an optimization with regard to the minimum amount of **5** necessary for successful ADIMET was of interest. The use of 1, 3, 5, and 20 equiv of **5** with 5 mol % $Mo(CO)_6$ on a very small scale gives polymers **4c** with P_n's of 16, 25, 29, and 41, respectively, and **4f** with P_n's of 27, 21, 24, and 32. In all eight cases the polymerization time had been 20 h. This result is in fair agreement with the hypothesis that a molybdenum carbyne of the structure $(Ar-O)_3Mo{\equiv}CR$ could be the source of the catalytic activity in these systems. We are currently investigating this topic, and a reasonable compromise for large scale applications seems to be the use of 5 equiv of phenolic activator per added equivalent of $Mo(CO)_6$.

Another important parameter is the nature of the phenolic activator. We investigated the effect of 4-chlorophenol (**5**), 4-trifluoromethylphenol (**6**), and 3,5-bis(trifluoromethyl)phenol (**7**) upon P_n. Utilization of 5 mol % of $Mo(CO)_6$ with 100 mol % of phenolic activator (20 h, 150 °C) furnished **4c** with P_n of 1.3×10^2 (**5**), 1.0×10^2 (**6**), and 1.3×10^2 (**7**), while **4f** was produced with P_n of 0.5×10^2 (**5**), 0.3×10^2 (**6**), and 0.4×10^2 (**7**). All of the tested phenolic activators work fine, but 4-chlorophenol, being by far the cheapest one, is the first choice for the metathesis of alkyl-substituted monomers **3**.

Alkoxy-Substituted PPEs. Alkoxy-substituted PPEs have recently found spectacular application in materials science[24] and it was of interest to see if the "instant" catalyst system would be capable of polymerizing alkoxy-substituted monomers **3** equally well. In a first experiment, we employed standard conditions with 4-chlorophenol as phenolic activator (at 130 °C) to polymerize **3i**, but only a small amount of low molecular weight oligomers was isolated (entry 26). Increasing the concentration of $Mo(CO)_6$ to 10 mol % and utilization of 4-(trifluoromethyl)phenol as phenolic activator (entry 27) furnished **4i** in which P_n exceeds 20 according to ^{1}H NMR spectroscopy. GPC gives a much higher P_n of 65 (with $M_w/M_n = 2.5$), but that could be due to aggregation of **4i** already in dilute chloroform solution. An increase in temperature to 170 °C did not lead to higher molecular weight **4i** (entry 28). A ^{13}C NMR spectrum of the material produced at 170 °C indicates the occurrence of defects of unknown structure.

Discussion

The influence of reaction temperature, reaction time, phenolic activator, and substituents on the ADIMET polymerization of dipropynylated benzenes **3** is substantial. For all monomers **3**, polymers **4** form in high yield. In general the method works better for alkyl-substituted monomers **3** than for alkoxy-substituted ones. The lowest P_n observed (with exception of the preliminary studies for **4a**) is the one for **4g** with 20−40 repeating units. Generally P_n is higher and averages to 2×10^2. However some very high molecular weight materials have been obtained. All of the polymers (for an exception, see below) are bright yellow.

•Not too surprisingly, isopentyl-, ethylbutyl-, and cyclohexyl-substituted PPEs **4** are insoluble but form in high yield by ADIMET of the corresponding monomers **3**. Dihexyl-substituted PPE **4a** is moderately soluble, but for samples of **4a** with more than 100 repeating units, the solubilizing power of the linear C_6 chain is insufficient.

•Long linear (C_9, C_{12}) or branched 2-ethylhexyl solubilizing chains give PPEs with the highest molecular weights. An increase in the reaction temperature leads to an increased molecular weight. However at temperatures above 150 °C, the obtained polymer batches have a brownish or grayish appearance. This indicates the presence of defect structures in the polymer chains, which affect the conjugated system. In the case of the linear solubilizing chains, the cheap 4-chlorophenol (**5**) seems to be an excellent choice as phenolic activator. To specifically make high molecular weight PPEs **4** we suggest a combination of dodecyl side chains (**3c**), a temperature of approximately 150 °C, and a reaction time of 24 h.

•In the case of branched substituents the trimethylhexyl-substituted polymer **4g** is of low molecular weight. High molecular weight ethylhexyl-substituted **4f** is obtained at temperatures slightly above 150 °C but only with 4-trifluoromethylphenol as phenolic activator. Here, similar to the dodecyl-substituted **4c**, a reaction time of 24 h is optimal to obtain a high molecular weight.

•Small-scale polymerizations (<0.2 g), however, give material of lower P_n due to difficulties in efficiently removing butyne and somewhat lower concentration of the monomers.

Conclusion

The extremely simple and easily accessible catalyst system formed from $Mo(CO)_6$ and 4-chlorophenol in off-the-shelf 1,2-dichlorobenzene catalyzes the ADIMET of dipropynylated benzenes **3a**−**j** efficiently. The monomers **3** react in the ADIMET under concomitant evolution of butyne to the corresponding high molecular weight poly(*p*-phenyleneethynylene)s **4** in excellent to quantitative yields. According to ^{13}C NMR spectroscopy these polymers **4** are defect-free and display only propynyl end groups. With the herein described protocol for alkyne metathesis we have presented a simple and reliable method to obtain high-molecular weight PPEs **4**. *For the synthesis of alkyl-substituted PPEs **4**, alkyne metathesis is by far superior to the classic Pd-catalyzed couplings with respect to purity, yield, and molecular weight of the product.*

In future contributions, we will explore the role and nature of the phenolic activators with regard to polymerization efficiency, reaction temperature, and reaction time. We will utilize a combinatorial strategy.

Experimental Section

Molecular weight determinations were performed using a Waters Styragel HMW 6E (7.8 mm i.d. × 300 mm) GPC column (20 μm particles/10 μm frits) eluted with $CHCl_3$ at ambient temperature (flow rate of 1 mL/min). Solubility data for the polymers **4** are provided with respect to chloroform at ambient temperature (25 °C), unless otherwise stated. The term soluble means, in this regard, that all of the polymer **4** under discussion is soluble in a sufficient amount of chloroform after heating and recooling to ambient temperature. Molecular weight results were based on 10 polystyrene standards (M_w = 3 900 000, 1 980 000, 996 000, 629 000, 210 000, 70 600, 28 600, 10 900, 3000, and 1300) purchased from Waters (type SM-105). The ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker AM 300 MHz or a Varian Mercury 400 MHz spectrometer operating in the FT mode at 300 MHz (^{1}H) and 75.5 MHz

(^{13}C) and at 400 MHz (^1H) and 100.6 MHz (^{13}C). The ^1H chemical shifts are referenced to the residual proton peaks of $CDCl_3$ at δ 7.24 (vs TMS) and $C_2Cl_4D_2$ at δ 5.99 (vs TMS). The ^{13}C resonances are referenced to the central peak of $C_2Cl_4D_2$ at δ 73.8 (vs TMS) and $CDCl_3$ at δ 77.0 (vs TMS). The solid-state spectra were measured on a Bruker DSX 300 operating at 75 MHz. A cross-polarization pulse sequence was used with a 1-ms contact time and a 3-s recycle delay. The spinning speed (magic-angle spinning) was 6 kHz. Elemental analyses were obtained from the Universität Mainz, Institut für Organische Chemie, Mainz, Germany.

General Procedure for Preparation of 1a−i.[1] Under nitrogen, 1 equiv of 1,4-dichlorobenzene and 0.1−1 mol % of $dpppNiCl_2$ (dppp = 1,3-bis(diphenylphosphino)propane) was slowly added to a solution of 2.5 equiv of alkylmagnesiumbromide in ethyl ether. The reaction mixture was refluxed for 48 h. The mixture is poured onto ice, diluted HCl was added, the organic layer was separated and washed neutral with H_2O (3 × 100 mL), and the aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. Evaporation of solvent furnishes viscous liquids which were purified by distillation.

1,4-Dihexylbenzene (1a). Application of the general procedure to 1,4-dichlorobenzene (118 g, 0.803 mol), $dpppNiCl_2$ (1.03 g, 1.89 mmol), and hexylmagnesium bromide {Mg (54.0 g, 2.20 mol), 1-bromohexane (309 g, 1.87 mol) in 1 L of ethyl ether} gives **1a** as a colorless oil (168 g, 85%); bp 112 °C (0.05 mbar). ^1H NMR ($CDCl_3$): δ 7.13 (s, 4H), 2.61 (t, 4H), 1.64 (m, 4H), 1.35 (m, 12 H), 0.93 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.1, 128.3, 35.7, 31.9, 31.7, 29.2, 22.8, 14.2.

1,4-Dinonylbenzene (1b). Application of the general procedure to 1,4-dichlorobenzene (35.3 g, 0.240 mol), $dpppNiCl_2$ (0.308 g, 0.565 mmol), and a Grignard solution {Mg (13.4 g, 0.551 mol), 1-bromononane (100 g, 0.48 mol) in 200 mL of ethyl ether} gives **1b** as a colorless oil (84 g, 84%). ^1H NMR ($CDCl_3$): δ 7.09 (s, 4H), 2.57 (t, 4H), 1.61 (m, 4H), 1.33−1.28 (m, 24H), 0.91 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.8, 128.1, 35.8, 32.2, 31.8, 29.9, 29.8, 29.7, 29.6, 22.9, 14.3.

1,4-Didodecylbenzene (1c). Application of the general procedure to 1,4-dichlorobenzene (118 g, 0.800 mol), $dpppNiCl_2$ (1.03 g, 1.89 mmol), and a Grignard solution {Mg (54.0 g, 2.20 mol), 1-bromododecane (572 g, 2.30 mol) in 1 L of ethyl ether} gives **1c** as a colorless oil (272 g, 82%). ^1H NMR ($CDCl_3$): δ 7.21 (s, 4H), 2.70 (t, 4H), 1.74 (m, 4H), 1.42 (bs, 36H), 1.04 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.1, 128.2, 35.6, 32.0, 31.6, 29.7, 29.6, 29.4, 22.7, 14.1.

1,4-Bis-(3-methyl)butylbenzene (1d). Application of the general procedure to 1,4-dichlorobenzene (118 g, 0.803 mol), $dpppNiCl_2$ (1.03 g, 1.89 mmol), and a Grignard solution {Mg (54.0 g, 2.20 mol), 1-bromo-3-methylbutane (332 g, 2.20 mol) in 1 L of ethyl ether} gives **1d** as a clear oil (163 g, 93%). ^1H NMR ($CDCl_3$): δ 7.19 (s, 4H), 2.70 (t, 4H), 1.73 (m, 2H), 1.61 (m, 4H), 1.06 (d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.5, 128.4, 41.0, 33.1, 27.6, 23.8. MS (GC, no heat): m/z 218 (M^+).

1,4-Bis-(2-ethyl)butylbenzene (1e). Application of the general procedure to 1,4-dichlorobenzene (13.1 g, 89.2 mmol), $dpppNiCl_2$ (97 mg, 0.18 mmol), and a Grignard solution {Mg (4.34 g, 179 mmol), 1-bromo-2-ethylbutane (29.5 g, 179 mmol) in 200 mL of ethyl ether}, after distillation under vacuum (88 °C, 0.5 mbar), provides **1e** as a clear oil (8.80 g, 40%). ^1H NMR ($CDCl_3$): δ 7.16 (s, 4H), 2.60 (t, 4H), 1.59 (m, 2H), 1.41 (m, 8H), 0.98 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.7, 128.7, 42.6, 39.3, 25.0, 10.9. MS: m/z 246 (M^+).

1,4-Bis-(2-ethyl)hexylbenzene (1f). Application of the general procedure to 1,4-dichlorobenzene (7.50 g, 51.0 mmol), $dpppNiCl_2$ (55 mg, 0.10 mmol), and a Grignard solution {Mg (2.48 g, 0.102 mol), 1-bromo-2-ethylhexane (16.8 g, 0.102 mol) in 200 mL of ethyl ether} followed by distillation under vacuum (190 °C, 0.4 mbar) provides **1f** as a clear oil (11.7 g, 76%). ^1H NMR ($CDCl_3$): δ 7.20 (s, 4H), 2.67 (d, 4H), 1.73 (m, 2H), 1.45 (m, 16H), 1.04 (t, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.6, 128.7, 41.2, 39.5, 32.5, 29.0, 25.6, 23.1, 14.2, 10.9.

1,4-Bis(3,5,5-trimethyl)hexylbenzene (1g). Application of the general procedure to 1,4-dichlorobenzene (36.8 g, 0.250 mol), $dpppNiCl_2$ (0.320 g, 0.588 mmol), and a Grignard-solution {Mg (13.6 g, 0.559 mol) and 1-bromo-3,5,5-trimethylhexane (109 g, 0.489 mol) in 200 mL of diethyl ether} gives **1g** as a colorless oil (53.0 g, 49%).

1-Bromo-(*S*)-(+)-3,7-dimethyloctane. (*S*)-(+)-Citronellylbromide (2.09 g, 9.50 mmol) and 10% palladium on charcoal (0.764 g) in 100 mL of ethanol are shaken under 50 psi of hydrogen for 14 h. After filtration over Celite and evaporation of solvent, distillation (30−40 °C, 0.1 mbar) provides a colorless liquid (1.91 g, 91%). ^1H NMR ($CDCl_3$): δ 3.41 (t, 2H), 1.14−1.87 (m, 10H), 0.88 (d, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 40.0, 39.08, 36.63, 32.04, 31.57, 27.86, 24.47, 22.63, 22.53, 18.91. MS (EI, no heat): m/z 221 (M^+).

1,4-Bis[(*S*)-(+)-3,7-dimethyloctyl]benzene (1h). Application of the general procedure to 1,4-dichlorobenzene (1.00 g, 6.75 mmol), $dpppNiCl_2$ (7 mg, 0.01 mmol), and a Grignard solution {Mg (0.328 g, 13.5 mmol), 1-bromo-(*S*)-(+)-3,7-dimethyloctane (2.98 g, 13.5 mmol) in 200 mL of ethyl ether}, followed by distillation under vacuum (195 °C, 0.1 mbar) provides **1h** as a clear oil (4.01 g, 83%).

1,4-Bis-(3-methyl)butyloxybenzene (1i). A suspension of KOH pellets (120 g, 2.14 mol) in 600 mL of DMSO is stirred under N_2 for 1 h. Hydroquinone (27.5 g, 0.250 mol) and 1-bromohexane (151 g, 1.00 mol) are added, and the reaction mixture is stirred for 14 h. The mixture is poured onto ice, the organic layer collected, and the aqueous layer extracted with 3 × 100 mL of hexanes. The combined organic layers are dried over $MgSO_4$. Evaporation of solvent and recrystallization from ethanol gives **1i** (48.0 g, 77%). ^1H NMR ($CDCl_3$): δ 6.81 (s, 4H), 3.92 (m, 4H), 1.81 (m, 2H), 1.65 (m, 4H), 0.95 (d, 12 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.2, 115.4, 67.0, 38.2, 25.1, 22.7.

1,4-Dicyclohexylbenzene (1j). Application of the general procedure to 1,4-dichlorobenzene (1.00 g, 6.75 mmol), $dpppNiCl_2$ (7 mg, 0.01 mmol), and a Grignard solution {Mg (0.328 g, 13.5 mmol), cyclohexylbromide (2.20 g, 13.5 mmol) in 200 mL of ethyl ether} provides **1j** as colorless material (1.21 g, 74%). ^1H NMR ($CDCl_3$): δ 7.14 (s, 4H), 2.49 (m, 2H), 1.91−1.75 (m, 8H), 1.48−1.25 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.3, 126.5, 44.2, 34.6, 27.1, 26.3. MS (no heat): m/z = 242 (M^+). Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.13; H, 10.88.

Preparation of the Diiodobenzenes. 1,4-Dihexyl-2,5-diiodobenzene (2a). In a round-bottomed flask are placed **1a** (98.6 g, 0.400 mol), KIO_4 (21.1 g, 91.7 mmol), I_2 (113 g, 0.444 mol), 600 mL of acetic acid, 160 mL of CCl_4, and 100 mL of concentrated H_2SO_4. This reaction mixture is stirred for 14 h at 90 °C. After the reaction is cooled to 4 °C, the product is filtered off. Recrystallization from ethanol provides colorless needles of **2a** (120 g, 60%); mp 47 °C. ^1H NMR ($CDCl_3$): δ 7.58 (s, 2H), 2.57 (t, 4H), 1.53, 1.32 (m, 16H), 0.88 (t, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.8, 139.3, 100.4, 39.9, 31.6, 30.2, 29.0, 22.6, 14.1.

1,4-Dinonyl-2,5-diiodobenzene (2b). Compound **1b** (28.8 g, 86.0 mmol), KIO_4 (18.0 g, 78.3 mmol), I_2 (40.6 g, 160 mmol), 120 mL of acetic acid, 100 mL of $CHCl_3$, 40 mL of concentrated H_2SO_4, and 40 mL of H_2O are stirred for 14 h at 90 °C. After the reaction is cooled to 4 °C, the mixture is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite solution, and extracted with 3 × 100 mL of hexanes. Recrystallization from ethanol provides colorless **2b** (22.3 g, 44%). ^1H NMR ($CDCl_3$): δ 7.57 (s, 2H), 2.57 (t, 4H), 1.54, 1.32−1.26 (m, 28H), 0.87 (t, 6H).

1,4-Didodecyl-2,5-diiodobenzene (2c). Compound **1c** (57.3 g, 138 mmol), KIO_4 (18.0 g, 78.3 mol), I_2 (40.6 g, 0.160 mol), 120 mL of acetic acid, 100 mL of $CHCl_3$, 40 mL of concentrated H_2SO_4, and 40 mL of H_2O are stirred for 14 h at 90 °C. After the reaction is cooled to 4 °C, the mixture is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite solution, and extracted with 3 × 100 mL of hexanes. Recrystallization from ethanol provides colorless **2c** (35.5 g, 39%). ^1H NMR ($CDCl_3$): δ 7.58 (s, 2H), 2.57 (t, 4H), 1.53 (bs, 4H), 1.25 (bs, 36H), 0.87 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.7, 139.2, 100.3, 39.9, 32.0, 30.3, 29.79, 29.78, 29.75, 29.66, 29.49, 29.45, 29.41, 22.8, 14.3.

1,4-Bis-(3-methyl)butyl-2,5-diiodobenzene (2d). Compound **1d** (25.0 g, 115 mmol), I_2 (32.0 g, 126 mmol), KIO_4 (8.70 g, 38.1 mmol) in 200 mL of acetic acid, 50 mL of CCl_4, and 30 mL of concentrated H_2SO_4 are heated to 80 °C for 14 h. After the reaction is cooled to 4 °C, the product precipitates and is filtered off. Recrystallization from ethanol gives pale pink needles of **2d** (33.0 g, 61%); mp 69−70 °C. ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 2H), 2.59 (t, 4H), 1.65 (m, 2H), 1.43 (m, 4H), 0.96 (t, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.7, 139.0, 100.1, 44.0, 37.8, 28.0, 22.5. MS (EI, no heat): *m*/*z* 470 (M^+).

1,4-Bis(2-ethyl)butyl-2,5-diiodobenzene (2e). Compound **1e** (8.00 g, 32.5 mmol), I_2 (8.43 g, 35.7 mmol), KIO_4 (7.40 g, 35.7 mmol) in 60 mL of acetic acid, 15 mL of CCl_4, and 10 mL of concentrated H_2SO_4 are heated to 125 °C for 36 h. After cooling to 4 °C, the mixture is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite solution, and extracted with 3 × 100 mL of hexanes. Filtration over silica gel (hexanes) and recrystallization from ethanol gave pale orange crystals of **2e** (9.47 g, 59%); mp 30 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 2H), 2.52 (d, 4H), 1.61 (m, 2H), 1.32 (m, 8H), 0.89 (t, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.5, 140.3, 100.6, 44.0, 40.6, 24.7, 10.8. MS: *m*/*z* 498 (M^+).

1,4-Bis(2-ethyl)hexyl-2,5-diiodobenzene (2f). Compound **1f** (47.7 g, 0.158 mol), KIO_4 (18.0 g, 78.3 mmol), I_2 (40.6 g, 0.160 mol), 120 mL of acetic acid, 100 mL of $CHCl_3$, 40 mL of concentrated H_2SO_4, and 40 mL of H_2O are stirred for 14 h at 90 °C. After the reaction is cooled to 4 °C, the mixture is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite solution, and extracted with 3 × 100 mL of hexanes. Recrystallization from ethanol provides colorless **2f** (26.1 g, 47%). ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 2H), 2.54 (d, 4H), 1.67 (t, 2H), 1.36−1.19 (m, 16H), 0.91−0.84 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.6, 140.4, 100.7, 43.9, 39.3, 32.2, 28.7, 25.5, 23.1, 14.2, 10.9.

1,4-Di(3,5,5-trimethylhexyl)-2,5-diiodobenzene (2g). Compound **1g** (53.0 g, 0.160 mol), KIO_4 (36.8 g, 0.160 mol), I_2 (75.0 g, 0.296 mol), 200 mL of acetic acid, 150 mL of $CHCl_3$, 60 mL of concentrated H_2SO_4, and 60 mL of H_2O are stirred for 16 h at 90 °C. The solution is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite, and extracted with 3 × 100 mL of hexanes. Recrystallization from ethanol provides **2g**. Yield: 43 g (82%).

1,4-Bis-(*S*)-(+)-3,7-dimethyloctyl-2,5-diiodobenzene (2h). Compound **1h** (3.96 g, 11.1 mmol), KIO_4 (1.50 g, 6.52 mmol), I_2 (6.25 g, 25.0 mmol), 20 mL of acetic acid, 1 mL of concentrated H_2SO_4, and 4 mL of H_2O are stirred for 12 h at 130 °C. After 6 h, 2 mL of CH_2Cl_2 is added. The solution is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite, and extracted with 3 × 100 mL of hexanes. Filtration over silica gel (hexanes) provides **2h** as an oil (8.64 g, 78%). ^{1}H NMR ($CDCl_3$): δ 7.59 (s, 2H), 2.64−2.55 (m, 4H), 1.57−1.48 (m, 4H), 1.40−1.20 (m, 8H), 1.19−1.06 (m, 8H), 0.96 (d, 6H), 0.89−0.84 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.0, 139.2, 100.3, 39.4, 37.7, 37.6, 37.1, 32.9, 28.1, 24.9, 22.9, 22.8, 19.8.

1,4-Bis(3-methyl)butyloxy-2,5-diiodobenzene (2i). Compound **1i** (48.0 g, 0.192 mol), KIO_3 (18.8 g, 87.9 mmol), I_2 (55.9 g, 0.220 mol), 1 L of acetic acid, 100 mL of H_2O, and 25 mL of concentrated H_2SO_4 are stirred for 14 h at 130 °C. Aqueous sodium sulfite solution is added until the brown color of iodine disappears. The mixture is poured onto ice-cold water. The aqueous layer is extracted with 3 × 200 mL of hexanes and the combined organic layers are dried over $MgSO_4$. Solvent evaporation and recrystallization from ethanol yields **2i** (53.1 g, 55%); mp 107−108 °C. ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 2H), 3.93 (m, 4H), 1.88 (m, 2H), 1.68 (m, 4H), 0.96 (d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.9, 122.7, 86.3, 68.7, 37.9, 25.1, 22.6.

1,4-Dicyclohexyl-2,5-diiodobenzene (2j). Compound **1j** (1.43 g, 5.90 mmol), KIO_4 (0.600 g, 2.61 mmol), I_2 (1.35 g, 5.32 mmol), 50 mL of acetic acid, 10 mL of $CHCl_3$, 10 mL of concentrated H_2SO_4, and 10 mL of H_2O are stirred for 14 h at 90 °C. After cooling to 4 °C the mixture is neutralized with sodium bicarbonate solution, washed with aqueous sodium sulfite solution, extracted with 3 × 50 mL of hexanes. Recrystallization from ethanol provides colorless **2j** (0.641 g, 22%). ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 2H), 2.64 (m, 2H), 1.85 (m, 4H), 1.79−1.74 (m, 8H), 1.46−1.22 (m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.6, 137.1, 101.7, 47.9, 33.5, 26.8, 26.1. MS (heat to 100): *m*/*z* 494 (M^+). Anal. Calcd for $C_{18}H_{24}I_2$: C, 43.75; H, 4.89. Found: C, 43.86; H, 4.70.

General Procedure for the Preparation of the Dipropynylbenzenes. A 250-mL flame-dried Schlenk flask containing 1,4-diiodo-2,5-dialkylbenzene (**2**) (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.351 g, 0.500 mmol), and CuI (0.190 g, 1.00 mmol) is degassed and evacuated. After the addition of 1 atm of propyne, piperidine (25 mL) is introduced into the reaction vessel via syringe through a septum. A white precipitate forms, and the clear green solution changes its color to yellow. One atmosphere of propyne is added after 2 and 4 h, respectively. The reaction mixture is stirred for a total of 7 h. For workup, 50 mL of hexanes and 50 mL of H_2O are added to the solution, and the aqueous layer is extracted with 3 × 50 mL of hexanes. The combined organic layers are washed with 3 × 50 mL of H_2O and dried over $MgSO_4$. Evaporation of solvent yields a crude product, which is purified via filtration through a silica gel column with hexanes or hexanes/CH_2Cl_2 as eluent followed by recrystallization from ethanol.

2,5-Dihexyl-1,4-dipropynylbenzene (3a). Application of the general procedure to **2a** (4.98 g, 10.0 mmol) furnishes colorless needles of **3a** (2.83 g, 88%; eluent hexanes; recrystallization); mp 44 °C. ^{1}H NMR ($CDCl_3$): δ 7.15 (s, 2H), 2.64 (t, 4H, J = 7.7 Hz), 2.07 (s, 6H), 1.58 (m, 4H), 1.31 (m, 12H), 0.88 (t, 6H, J = 6.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.8, 132.2, 122.6, 89.7, 78.6, 33.8, 31.7, 30.4, 29.1, 22.6, 14.1, 4.49. MS: *m*/*z* 322 (M^+). Anal. Calcd for $C_{24}H_{34}$: C, 89.45; H, 10.63. Found: C, 88.74; H, 10.69.

2,5-Dinonyl-1,4-dipropynylbenzene (3b). Application of the general procedure to **2b** furnishes colorless **3b** (83%; eluent hexanes; recrystallization); mp 62 °C. ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 2H), 2.65 (t, 4H), 2.07 (s, 6H), 1.62−1.55 (m, 4H), 1.32−1.26 (m, 24H), 0.88 (t, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.6, 132.0, 122.4, 89.6, 78.6, 33.9, 32.0, 30.5, 29.63, 29.57, 29.5, 29.45, 22.8, 14.2, 4.59. MS (heat to 100 °C): *m*/*z* 406 (M^+).

2,5-Didodecyl-1,4-dipropynylbenzene (3c). Application of the general procedure to **2c** furnishes colorless **3c** (96%; eluent hexanes); mp 66−68 °C. ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 2H), 2.63 (t, 4H), 2.06 (s, 6H), 1.57 (m, 4H), 1.30−1.18 (m, 12H), 0.87 (t, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.6, 132.0, 122.4, 89.6, 78.6, 33.9, 32.0, 30.5, 29.79, 29.75, 29.68, 29.57, 29.51, 29.45, 22.8, 22.8, 14.2, 4.61. MS (heat to 200 °C): *m*/*z* 491 (M^+). Anal. Calcd for $C_{36}H_{58}$: C, 88.09; H, 11.91. Found: C, 88.07; H, 11.82.

2,5-Bis-(3-methyl)butyl-1,4-dipropynylbenzene (3d). Application of the general procedure to **2d** (9.40 g, 20.0 mmol) furnishes colorless **3d** (4.30 g, 73%; eluent hexanes; recrystallization); mp 46−47 °C. ^{1}H NMR ($CDCl_3$): δ 7.17 (s, 2H), 2.66 (m, 4H), 2.08 (s, 6H), 1.61 (m, 2H), 1.47 (m), 0.95 (d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.9, 131.9, 122.4, 89.7, 78.5, 40.0, 31.8, 28.0, 22.6, 4.56. MS: *m*/*z* 294 (M^+).

2,5-Bis-(2-ethyl)butyl-1,4-dipropynylbenzene (3e). Application of the general procedure to **2e** (4.98 g, 10.0 mmol) furnishes pale pink needles of **3e** (1.16 g, 36%; eluent hexanes−CH_2Cl_2 (4:1); recrystallization); mp 54−55 °C. ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 2H), 2.58 (t, 4H), 2.06 (s, 6 H), 1.60 (m, 2H), 1.31 (m, 8H), 0.89 (t, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.6, 133.0, 122.4, 89.6, 78.8, 41.6, 37.6, 25.1, 10.9, 4.46. MS: *m*/*z* 322 (M^+). Anal. Calcd for $C_{24}H_{34}$: C, 89.38; H, 10.62. Found: C, 88.22; H, 10.18.

2,5-Bis(2-ethyl)hexyl-1,4-dipropynylbenzene (3f). Application of the general procedure to **2f** (2.70 g, 4.91 mmol) furnishes **3f** (1.41 g, 76%; eluent hexanes); mp 64−65 °C. ^{1}H NMR ($CDCl_3$): δ 7.11 (s, 2H), 2.56 (m, 4H), 2.05 (s, 6H), 1.63 (m, 2H), 1.27 (m, 16 H), 0.85 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.8, 133.2, 122.6, 89.7, 79.0, 40.2, 38.3, 32.7, 29.1, 25.7, 23.2, 14.3, 11.0, 4.63. MS: *m*/*z* 378 (M^+). Anal. Calcd for $C_{28}H_{42}$: C, 88.82; H, 11.18. Found: C, 88.49; H, 11.29.

2,5-Bis(3,5,5-trimethyl)hexyl-1,4-dipropynylbenzene (3g). Application of the general procedure to **2g** (14.5 g, 24.9 mmol) furnishes colorless **3g** (9.91 g, 68%; eluent hexanes; recrystallization); mp 66−67 °C. ^{1}H NMR ($CDCl_3$): δ 7.14 (s,

2H), 2.62 (m, 4H), 2.05 (s, 6H), 1.58−1.52 (m, 2H), 1.50−1.35 (m, 4H), 1.28 (dq, 4H), 1.06 (dq, 4H), 0.97 (d, 6H), 0.88 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.0, 131.9, 122.4, 89.6, 78.5, 51.2, 40.6, 32.0, 31.2 30.1, 29.6, 22.7, 4.60. MS: *m/z* 407 (M^+). Anal. Calcd for $C_{30}H_{46}$: C, 88.60; H, 11.40. Found: C, 88.84; H, 11.03.

2,5-Bis(*S*)-(+)-(3,7-dimethyloctyl)-1,4-dipropynylbenzene (3h). Application of the general procedure to **2h** (3.88 g, 8.92 mmol) furnishes **3h** as a viscous liquid (2.37 g, 60%; eluent hexanes). ^1H NMR ($CDCl_3$): δ 7.17 (s, 2H), 2.74−2.58 (m, 4H), 2.07 (s, 6H), 1.64−1.23 (m, 16H), 1.18−1.11 (m, 4H), 0.95 (d, 6H, J = 6.4 Hz), 0.88 (d, 12H, J = 6.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.0, 132.0, 122.5, 89.5, 78.6, 39.4, 38.1, 37.2, 32.9, 31.6, 28.1, 24.9, 22.8, 22.7, 19.8, 4.56. MS: *m/z* 434.5 (M^+). Anal. Calcd for $C_{32}H_{50}$: C, 88.40; H, 11.59. Found: C, 88.38; H, 11.65.

2,5-Bis-(3-methyl)butyloxy-1,4-dipropynylbenzene (3i). Application of the general procedure to **2i** (4.74 g, 10.0 mmol) furnishes **3i** (2.13 g, 69%; eluent hexanes−CH_2Cl_2 (5:2); recrystallization); mp 72−73 °C. ^1H NMR ($CDCl_3$): δ 6.84 (s, 2H), 3.95 (m, 4H), 2.07 (s, 6H), 1.83 (m, 2H), 1.69 (m), 0.95 (d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.5, 117.4, 113.9, 90.9, 76.0, 68.2, 38.0, 25.2, 22.7, 4.73. MS:*m/z* 326 (M^+). Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.44; H, 9.09. Found: C, 80.44; H, 9.20.

2,5-Dicyclohexyl-1,4-dipropynylbenzene (3j). Application of the general procedure to **2j** (2.33 g, 4.71 mmol) furnishes **3j** (1.17 g, 78%; eluent hexanes). ^1H NMR ($CDCl_3$): δ 7.19 (s, 2H), 2.92 (m, 2H), 2.08 (s, 6H), 1.83 (t, 8H), 1.21−1.45 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.1, 129.3, 122.2, 89.7, 78.6, 41.5, 33.5, 27.1, 26.4, 4.66. MS (heat to 100): *m/z* 318 (M^+). Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49. Found: C, 90.47; H, 9.54.

General Procedure for the Polymerizations. In a typical reaction, **3** (0.500 g) and the catalyst system consisting of $Mo(CO)_6$ (5 mol %)/substituted phenol (1 equiv of either *p*-chlorophenol or *p*-trifluorocresol) are dissolved in 30 mL of *o*-dichlorobenzene and stirred at temperatures between 120 and 170 °C overnight, removing butyne by a slow stream of nitrogen. The formed fluorescent solution is cooled and any precipitated polymer dissolved by the addition of CH_2Cl_2. The organic layer is washed with 100 mL of each H_2O, 10% NaOH, and 25% HCl. Addition of methanol precipitates yellow polymer **4,** which is filtered and vacuum-dried. For yields and amounts, see Table 1.

Polymer 4a. Partially soluble in chloroform, fully soluble in hot 1,2-dichloroethane. ^1H NMR ($CDCl_3$): δ 7.38 (bs, 2H), 2.83 (bs, 4H), 2.10 (s), 1.71 (bs, 4H), 1.34 (bs, 12H), 0.89 (bs, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.8, 132.3, 122.7, 93.1, 34.3, 32.0, 30.8, 29.4, 22.8, 14.3, 1.20. ^{13}C CP MAS NMR: δ 142.6, 132.5, 122.8, 95.0, 33.7, 23.6, 14.7. Anal. Calcd for $n \times (C_{20}H_{28}) + C_4H_6$: C, 89.38; H, 10.62. Found: C, 87.45; H, 9.53.

Polymer 4b. Soluble. ^1H NMR ($CDCl_3$): δ 7.40 (s), 2.85 (bs), 2.12 (s, propyne end groups), 1.74 (bs), 1.58−1.28 (bs), 0.91−0.88 (bs). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.8, 132.3, 122.7, 93.1, 34.3, 32.0, 30.9, 29.8, 29.5, 22.8, 14.2. Anal. Calcd for $n \times (C_{20}H_{28}) + C_4H_6$: C, 89.38; H, 10.62. Found: C, 86.95; H, 10.62.

Polymer 4c. Soluble. ^1H NMR ($CDCl_3$): δ 7.36 (bs, 2H), 2.82 (bs, 4H), 1.71 (bs), 1.54 (bs), 1.39−1.24 (bs), 0.88−0.85 (bs). $^{13}C\{^1H\}$ NMR ($C_2Cl_4D_2$, 120 °C): δ 141.8, 132.2, 122.9, 93.3, 34.0, 31.6, 30.3, 29.39, 29.36, 29.3, 29.0, 22.3, 13.6. ^{13}C CP MAS NMR: δ 143.7, 132.8, 123.1, 95.2, 33.0, 23.8, 14.4. Anal. Calcd for $n \times (C_{32}H_{52}) + C_4H_6$: C, 88.09; H, 11.91. Found: C, 87.28; H, 11.02.

Polymer 4d. Insoluble. ^{13}C CP MAS NMR: δ 143.7, 132.7, 122.9, 94.3, 42.7, 32.9, 29.3, 23.8. Anal. Calcd for $n \times (C_{18}H_{24}) + C_4H_6$: C, 81.93; H, 9.37. Found: C, 83.31; H, 8.94.

Polymer 4e. Sparingly soluble. ^{13}C CP MAS NMR: δ 142.7, 134.5, 123.5, 95.9, 41.5, 25.5, 11.3. Anal. Calcd for $n \times (C_{20}H_{28}) + C_4H_6$: C, 89.38; H, 10.62. Found: C, 87.82; H, 10.52.

Polymer 4f. Soluble. ^1H NMR ($CDCl_3$): δ 7.35 (s, 2H), 2.77 (bs, 4H), 2.10 (s, propyne end groups), 1.81 (bs, 2H), 1.38−1.29 (m, 16H), 0.92, 0.85 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.9, 133.2, 123.0, 93.4, 40.4, 38.7, 32.6, 28.9, 25.8, 23.2, 14.3, 11.0, 4.75, 1.16. Anal. Calcd for $n \times (C_{24}H_{36}) + C_4H_6$: C, 88.82; H, 11.18. Found: C, 87.38; H, 11.49.

Polymer 4g. Soluble. ^1H NMR ($CDCl_3$): δ 7.36 (s, 2H), 2.80 (bs, 4H), 2.09 (s), 1.60−1.32 (bs), 1.24 (bs), 1.13−0.96 (bs), 0.91−0.83 (bs). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.1, 132.2, 122.7, 92.9, 51.3, 40.7, 32.2, 31.2, 30.2, 29.8, 22.9. Anal. Calcd for $n \times (C_{26}H_{40}) + C_4H_6$: C, 88.60; H, 11.40. Found: C, 87.95; H, 10.95.

Polymer 4h. Soluble. ^1H NMR ($CDCl_3$): δ 7.37 (bs, 2H), 2.87, 2.79 (bs, 4H), 1.72 (bs, 4H), 1.50, 1.34, 1.12, 0.98 (bs, 16H), 0.84 (bs, 18H), 0.07 (s, propyne end groups). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.1, 132.3, 122.7, 93.0, 39.4, 38.3, 37.4, 33.1, 32.0, 28.1, 24.9, 22.8, 22.7, 19.9, 1.16. Anal. Calcd for $n \times (C_{28}H_{44}) + C_4H_6$: C, 88.41; H, 11.59. Found: C, 87.34; H, 11.60.

Polymer 4i. Soluble. ^1H NMR ($CDCl_3$): δ 7.00 (s, 2H), 4.04 (m, 4H), 2.15 (s, propyne end groups), 1.90 (m, 2H), 1.73 (m, 4H), 0.98 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.2, 116.8, 114.0, 86.2, 86.0, 38.0, 25.2, 22.7. Anal. Calcd for $n \times (C_{18}H_{24}O_2) + C_4H_6$: C, 80.94; H, 9.26. Found: C, 77.28; H, 8.20.

Polymer 4j. Insoluble. Anal. Calcd for $n \times (C_{20}H_{24}) + C_4H_6$: C, 90.51; H, 9.49. Found: C, 87.98; H, 8.91.

Polymer 4k. Slightly soluble. ^1H NMR ($CDCl_3$): δ 7.39 (bs, 2H), 2.85 (bs, 4H), 2.11 (s), 1.71 (bs), 1.54, 1.43, 1.35 (bs, 12H), 0.99 (m), 0.90 (bs, 6H). ^{13}C CP MAS NMR: δ 142.9, 132.4, 122.8, 94.8, 32.7, 30.7, 23.2, 14.5. Anal. Calcd for $n \times [0.8 (C_{20}H_{28}) + 0.2 (C_{18}H_{24})] + C_4H_6$: C, 89.44; H, 10.56. Found: C, 88.39; H, 10.35.

Polymer 4l. Soluble. ^1H NMR ($CDCl_3$): δ 7.38 (s), 2.84 (bs), 2.10 (s, propyne end groups), 1.72 (bs), 1.42, 1.34, 1.25 (bs), 0.87 (bs). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 141.8, 132.3, 122.7, 93.1, 34.3, 32.0, 31.9, 30.8, 29.8, 29.5, 29.4, 22.8, 14.2. Anal. Calcd for $n \times [0.5 (C_{20}H_{28}) + 0.5 (C_{32}H_{52})] + C_4H_6$: C, 88.60; H, 11.40. Found: C, 87.34; H, 11.19.

Time Experiments. First, 5.00 g of **3c**, or **3f** (3.00 g) and the catalyst system consisting of $Mo(CO)_6$ (5 mol %) and 4-chlorophenol (1 equiv with respect to monomer **3**) were dissolved in 75 mL (50 mL) of *o*-dichlorobenzene and stirred at 150 °C, removing butyne by a slow stream of nitrogen. At given time intervals (see Figure 4), 5 mL of the formed fluorescent solution is withdrawn from the reaction mixture through a septum via syringe and cooled, and any precipitated polymer is dissolved by the addition of 50 mL of CH_2Cl_2. The organic layer of each aliquot is washed with 50 mL of each H_2O, 10% NaOH, and 25% HCl. Addition of methanol (250 mL) precipitates yellow polymer **1c,f**, which is filtered and vacuum-dried. All of the isolated polymers from the removed aliquots are fully soluble in halogenated organic solvents, allowing full characterization by GPC.

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