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Synthesis of Polyenes That Contain Metallocenes via the Living Polymerization of Ethynylferrocene and Ethynylruthenocene

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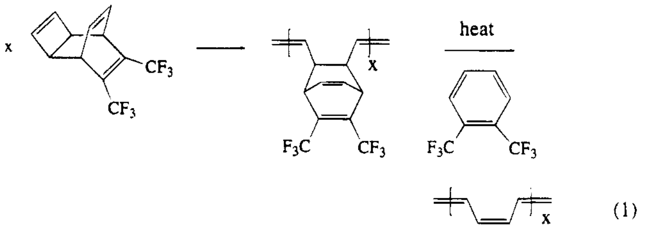
ABSTRACT: We describe the living polymerization of ethynylferrocene and ethynylruthenocene and the copolymerization of ethynylferrocene and TCDTF6 (TCDTF6 = 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]-deca-3,7,9-triene). In all cases $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ was the initiator that was employed. Charged systems were generated by terminating the living polymer with pyridinecarboxaldehyde followed by quaternizing the tertiary nitrogen with methyl iodide. Polyenes and copolyenes that contain up to ~50 double bonds are soluble. Charged polymers exhibit a more intense and red-shifted absorption. NMR studies suggest that ethynylferrocene adds to the initiator to give an unobservable intermediate α-substituted metallacyclobutene that opens to give the disubstituted (ferrocenyl/vinyl) propagating alkylidene. The structures of the first and second insertion products obtained by capping the chain with ferrocenecarboxaldehyde or pyridinecarboxaldehyde confirm that α addition takes place, a trans double bond is formed, and polymerization is virtually exclusively head-to-tail. Ethynylferrocene reacts extremely slowly with $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ via α addition and with $Mo(NAr)(CHCMe_2Ph)(OC_6F_5)_2$(quinuclidine) and $Mo(NAd)(CHCMe_2Ph)[OCH(CF_3)_2]_2$(2,4-lutidine) via β-addition.

Introduction

Nonlinear optical materials have considerable potential for frequency doubling, modulation, and switching, as well as other electronic applications.[1−7] Conjugated organometallic materials (such as polyenes) that contain metallocenes are believed to have some of the greatest potential for high second- and third-order nonlinearities for primarily three reasons: (i) metallocenes show M−L (metal-to-ligand) and L−M (ligand-to-metal) charge-transfer absorptions in the UV−vis region, transitions that are often associated with large second order nonlinearities; (ii) metallocenes often have high transition dipole moments, which lead to high second order nonlinearities; and (iii) metallocenes often are stable in oxidation states that differ by one electron and therefore can give rise to charged polymers. In donor−acceptor or charged systems β has been found to be proportional to $\sim N^3$ (N = number of double bonds in a polyene),[8] while γ is proposed[9] to be proportional to $\sim N^5$. The importance of electronic asymmetry in charged or donor−acceptor systems is well established; β consists of β_{add} and β_{CT}, the latter being affected most significantly by donor or acceptor substitution.[10] In general, the most desirable polyenes would have a high (effective) conjugation length, a low energy absorption with high molar extinction coefficient (ϵ) in the UV−vis region, and the possibility of donor/acceptor substitution or formation of charged systems by adding or removing electrons.

A logical approach to ferrocene-substituted polyenes is to polymerize ethynylferrocene. There have been several attempts to polymerize ethynylferrocene in a controlled way,[11−14] but none has produced polymer in high yield that has satisfactory and convincing physical properties, especially low PDI and good solubility. In all cases, trimers (1,3,5- and 1,2,4-triferrocenylbenzene), apparent oligomers with high polydispersities (5−10), or insoluble, brown, probably partially oxidized, poorly characterized polymers were obtained. One might expect polymerization of ethynylferrocene and ethynylruthenocene to be difficult, since the electron-releasing character of the metallocene is high, and metallocene-substituted terminal acetylenes therefore are more reactive than an all-carbon relative.

We have been exploring the use of initiators of the type $Mo(NR')(CHCMe_2Ph)(OR)_2$ (R′ = 2,6-i-$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$, or adamantyl; R = t-Bu, $CMe(CF_3)_2$)[15,16] for the synthesis of polyenes via living polymerization methods, either directly from alkynes[17−19] or indirectly via ROMP[20−22] using the "Feast" approach,[23,24] i.e., the synthesis of poly(TCDTF6) (TCDTF6 = 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene) and conversion of it to unsubstituted polyenes upon heating (eq 1). A necessary feature of a living polymerization system, at least if low polydispersity polymer is desired, is that there be only a single mode (rate) of chain growth. In the case of polymerization of alkynes by well-defined alkylidene complexes, either all "β addition" or all "α addition" would in theory be satisfactory (Scheme 1; P = polymer chain), but a polymerization reaction that proceeds via both types of chain growth would not. Recently all α addition was found to predominate when the alkoxide was small, R′ was large, and repulsion between the growing polymer chain and R′ was significant.[19] Although all α addition results in the formation of disubstituted propagating alkylidenes, such alkylidenes were found to be much more reactive than anticipated, and therefore suitable as intermediates in a polymerization reaction. The fact that Mo=C rotamers (e.g., syn and anti monosubstituted alkylidenes[25]) can form if the alkylidene is not symmetrically



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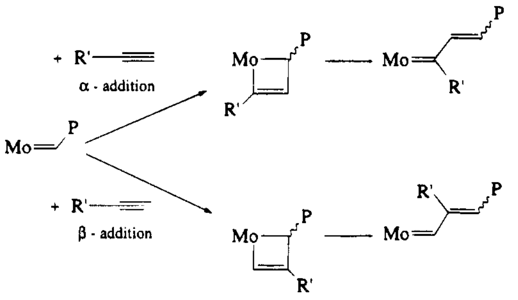
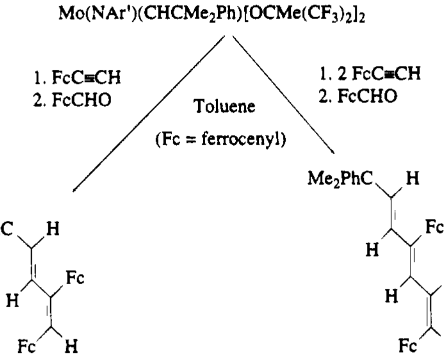
Scheme 1



Scheme 2



substituted, and that such rotamers could have dramatically different reactivities and rates of interconversion, further complicates the issue.

In this paper we report the synthesis of low-polydispersity "polyacetylenes" that contain ferrocene and ruthenocene as side groups via polymerization of ethynylferrocene or ethynylruthenocene, respectively, with $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$[26] as the initiator.

Results

Synthesis of Homopolymers. Upon addition of 1.25 equiv of ethynylferrocene to $Mo(NAr')(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ ($Ar' = 2,6\text{-}Me_2C_6H_3$), the initiator was consumed rapidly and resonances corresponding to first and second insertion products were observed. Addition of 10 equiv or more of ethynylferrocene caused these resonances to disappear. At no time were H_α alkylidene resonances observed that would be the consequence of β addition. If only 1 equiv of ethynylferrocene is added to the initiator, resonances for the first insertion product predominate. The first insertion product is characterized by two doublets at 7.01 and 6.17 ppm with $J = 16$ Hz, consistent with trans coupling of the olefinic protons in the $CH{=}CHCMe_2Ph$ group. Resonances for the ferrocenyl group were observed at 4.12 (t), 4.08 (s), and 4.03 (t) ppm, for the imido methyl groups at 2.42 ppm, and for the alkoxide methyl groups at 1.38 ppm. Addition of ferrocenaldehyde (in order to cleave off the organic chain in a Wittig-like reaction) and chromatography of the reaction mixture on silica gel gave the first insertion product (Scheme 2; Fc = ferrocenyl) in 65% yield. An analogous experiment in which 2 equiv of ethynylferrocene were added to the initiator followed by ferrocenaldehyde and chromatography gave the second insertion product (Scheme 2) in 36% yield. Insertion of ethynylferrocene into the $Mo{=}CHCMe_2Ph$ bond yields a trans double bond, according to the olefinic HH coupling in the first insertion product (16 Hz). The second insertion must also take place via α addition, since only one HH coupling (18 Hz) is observed. Therefore, we assume that only head-to-tail polymers will form as a consequence of solely α addition during the propagation step in a polymerization reaction. Although the "capped" first and second insertion products are drawn in the all-trans form and with the ferrocenyl group from ferrocenaldehyde trans to the ferrocenyl group on the next carbon atom, we actually can be certain only of the configuration of the "first" double bond formed as a consequence of addition of the first monomer to the initiator. No other capping products were observed. The good yields of the capped first and second insertion products suggest that the rate of initiation is at least competitive with the rate of propagation. Measurement of k_p/k_i[27] gave a value of 3.4. The fact that propagation is not slower than initiation is somewhat surprising in view of the disubstituted nature of the propagating alkylidene. Evidently, the electron-rich nature of ethynylferrocene (and the disubstituted alkylidene prepared from it) compensates for unfavorable sterics associated with a disubstituted alkylidene. High reactivity of the disubstituted alkylidene also accounts for its facile reaction with benzaldehyde and ferrocenaldehyde in Wittig-like "capping" reactions.

Table 1. Summary of Polymerization Results for Ethynylferrocene[a]

solvent	equiv	M_w/M_n	yield (%)	M_n(LS)	M_{calc}	time (h)
toluene	1	1[b]	65		540	1
toluene	2	1[b]	36		750	1
toluene	10	1.17	60	2300	2430	2.5
toluene	20	1.29	75	5400	4530	2.5
toluene	30	1.26	>95	6800	6630	2.5
toluene	40	1.24	>95	9800	8730	2.5
toluene	50[c]	1.45	>95	10600	10830	2.5
toluene	60[c]	1.34	>95	9800	12930	2.5
benzene	10	1.55	70	2800	2430	2
benzene	20	1.26	90	3700	4530	2
benzene	30	1.18	>95	8300	6630	2.5
benzene	40	1.06	>95	7900	8730	2.5
benzene	50	1.30	>95	9500	10830	2.5
benzene	60[c]	1.28	>95	13800	12930	2.5
THF	20	1.27	30	4700	4530	22
THF	30	1.13	>95	9300	6630	22
THF	40	1.20	>95	8500	8730	22
THF	50	1.24	>95	9900	10830	22
THF	70[c]	1.75	>95	14600	15030	22
benzene	10[d]	1.62	40	2300	2323	2.5
benzene	20[d]	1.26	80	4500	4423	2.5
benzene	30[d]	1.24	>95	6100	6523	2.5
benzene	40[d]	1.17	>95	10200	8623	2.5
benzene	50[d]	1.20	>95	9400	10723	2.5

[a] Capped with ferrocenaldehyde, except where noted; LS = by light scattering at 690 nm. [b] Isolated insertion product; see text and the Experimental Section. [c] Poor solubility. [d] Capped with pyridine-4-carboxaldehyde.

Soluble homopolymers of ethynylferrocene can be prepared that contain up to 40 equiv of monomer (Table 1). Beyond that point solubility decreases and the polymer begins to precipitate during the polymerization reaction. The yield of the 10- and 20-mers were limited by the fact that they could not be precipitated efficiently by adding pentane to the toluene reaction solvent. The absolute molecular weights, as determined by light scattering (at 690 nm), in general agree with M_n calculated on the basis of the number of monomers employed, except in some cases (the 60-mer especially) where polymer begins to precipitate during the reaction.

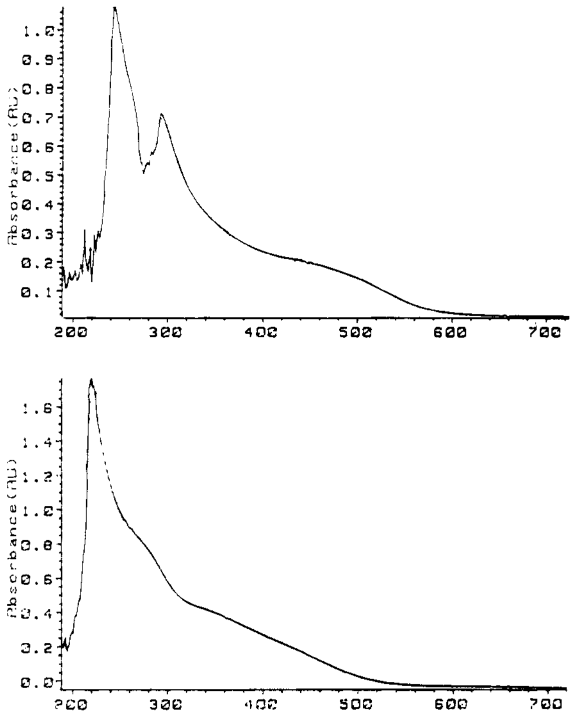


Figure 1. UV/vis spectra of poly(FcC$\equiv$CH)$_{60}$ (top) and poly(RcC$\equiv$CH)$_{40}$ (bottom) in THF (Fc = ferrocenyl, Rc = ruthenocenyl).

Polydispersities generally are less than 1.3. All polymers show absorptions characteristic of ferrocene at 225 and 280 nm, along with relatively broad absorptions out to slightly beyond 600 nm (Figure 1, top). Absorptions in the region 350–600 nm can be ascribed to what are most likely a complex mixture of $\pi-\pi^*$ transitions in the polymer backbone as well as the metallocene. Apparently 1,3-steric interactions between metallocenes prevent a more efficient π overlap in the backbone of the polyene and a more well-defined, intense, red-shifted absorption ascribable to a highly conjugated polyene backbone. Poly(ethynylferrocene) is soluble in THF, chloroform, and methylene chloride up to approximately the 60-mer. Homopolymers prepared from more than 100 equiv of ethynylferrocene are insoluble in common organic solvents.

Polymerization of ethynylferrocene in benzene or THF produced polymers that were virtually identical to those produced in toluene (Table 1). However, the rate of polymerization in THF was much slower than in toluene or benzene as a consequence of competitive inhibition by THF coordinating to the metal.[15] Therefore, reaction times had to be increased by an order of magnitude in order to produce polymer in high yield.

A plot of the molecular weights for all homopolymers (as determined by light scattering at 690 nm) versus number of monomers employed is shown in Figure 2. Good agreement between experimental and theoretical molecular weights is further evidence that the polymerization reaction is well-behaved and living. The origin of the larger than expected PDI values for a "perfect" living system (typically 1.05–1.10) is not known. However, it should be noted that the two substituents on the disubstituted propagating alkylidene are different. Therefore, "rotamers" are possible whose reactivities are not likely to be the same.[25] However, we would not expect the reactivities of such rotamers to differ to as great a degree as they do for *terminal* alkylidene (syn and anti) rotamers.[25]

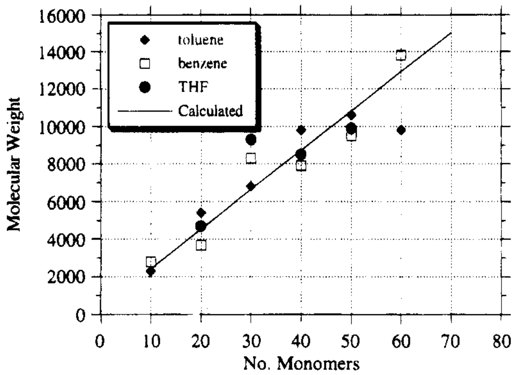


Figure 2. Plot of absolute molecular weight versus equivalents of monomer for poly(ethynylferrocene) prepared in toluene, THF, or benzene.

Table 2. Molar Extinction Coefficient of Polyethynylferrocene in THF[a]

equiv	ϵ 280 nm[b]	ϵ 480 nm[b]
10[c]	3×10^4	8×10^3
20	5.7×10^4	1.5×10^4
30	1.1×10^5	2.8×10^4
40	1.2×10^5	3.4×10^4
50	1.6×10^5	4.3×10^4
60	2.0×10^5	5.2×10^4
70	2.3×10^5	7.1×10^4

[a] Polymerization solvent = THF, except where noted. [b] L/mol·cm. [c] Polymerization solvent = toluene.

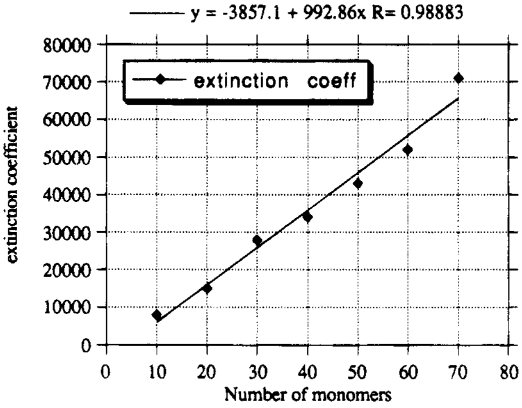


Figure 3. Plot of the molar extinction coefficient at 480 nm versus monomer equivalents (from data in Table 2).

Table 2 lists the molar extinction coefficients at 280 and 480 nm for the 10-mers through the 70-mers. The values at 480 nm are plotted versus the number of monomers in Figure 3. A slope of approximately 1 suggests that ϵ depends solely on the number of monomers (double bonds) in the polyene chain, i.e., any contributions to ϵ that could be ascribed to long-range phenomena are small.

Homopolymers of ethynylferrocene (10–50-mers; Table 1) also were prepared where the capping group was derived from pyridine-4-carboxaldehyde. In order to prove that chain termination by pyridine-4-carboxaldehyde actually takes place, the capped "2-mer" was isolated in 33% yield by chromatographing the crude reaction mixture on silica gel and recrystallizing the product from a mixture of diethyl ether and pentane. Proton NMR spectra confirm formation of a trans double bond (J = 16 Hz) as a consequence of the first insertion reaction. The lack of any other HH coupling confirms head-to-tail propagation in the second insertion step (eq

Table 3. Summary of Polymerization Results for Ethynylruthenocene[a]

solvent	equiv	M_w/M_n	yield (%)	M_n(LS)	M_{calcd}	rxn time
benzene	20	1.14	80	6700	5323	2.5
benzene	30	1.24	>95	8200	7873	2.5
benzene	45	1.24	>95	12600	11658	2.5
benzene	50	1.14	>95	14200	12923	2.5
benzene	60	1.19	99	16400	15473	2.5

[a] Capped with pyridine-4-carboxaldehyde.

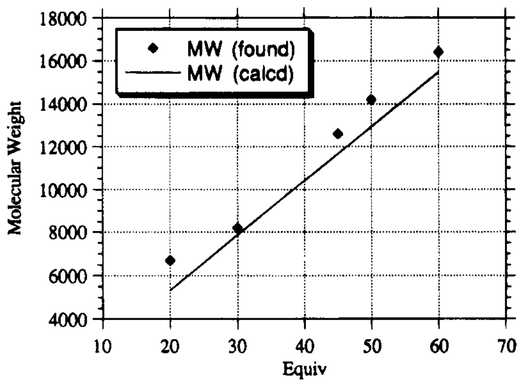
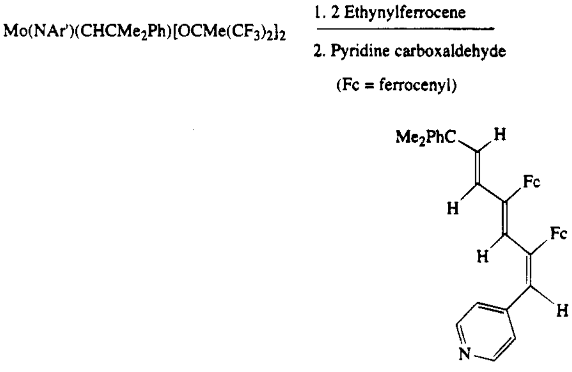


Figure 4. Plot of the absolute molecular weight of poly(ethynylruthenocene) versus equivalents of monomer (from data in Table 3).

2). Only one type of terminal double bond (arbitrarily shown with the pyridine trans to the ferrocene) is observed.



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Ethynylruthenocene also was polymerized in benzene and capped with pyridine-4-carboxaldehyde (Table 3). According to NMR studies, the polymerization is entirely analogous to that of ethynylferrocene, i.e., polymerization proceeds solely by α addition, and the first double bond that is formed as a consequence of opening the metallacyclobutene ring is trans (J_{HH} = 17 Hz). The ratio of k_p to k_i (2.6) is approximately the same as the k_p/k_i observed for ethynylferrocene. The polydispersities observed for poly(ethynylruthenocene) are slightly lower and more consistent than those for poly(ethynylferrocene), and a plot of absolute molecular weight versus number of monomers employed is again linear (Figure 4), consistent with a living polymerization. In poly(ethynylruthenocene) the low-energy absorptions that can be ascribed in part to $\pi-\pi^*$ transitions in the polyene backbone as well as in the metallocene part are blue-shifted (Figure 1, bottom) compared to where they are in poly(ethynylferrocene). Similar trends in UV/vis data for ferrocene and ruthenocene systems were observed by Marder and co-workers.[28]

Synthesis of Copolymers. We have shown recently that it is possible to prepare copolymers from diethyl dipropargyl malonate and TCDTF6 (TCDTF6 = 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene[29]) with Mo[OCMe(CF$_3$)$_2$]$_2$ initiators in 1,2-dimethoxyethane,[18] which upon heating give "hybrid" polyenes that are more fully conjugated by virtue of the presence of at least two unsubstituted double bonds between sterically more bulky monomers in the polyene chain. (TCDTF6 is the source of four unsubstituted olefinic carbon atoms (eq 1).) We show here that what appear to be largely alternating copolymers of ethynylferrocene and TCDTF6 can be prepared in THF and converted into highly conjugated, soluble "copolyenes". Attempts to prepare the longer copolymers in toluene were not as successful, as evidenced by large PDI values.

Copolymers were prepared by adding a mixture of ethynylferrocene and TCDTF6 to the initiator in THF all at once or in two instances in portions of a mixture of 5 equiv of each. The polymers were capped with pyridine-4-carboxaldehyde and heated to 70 °C in order to convert them into copolyenes (Table 4). For short-chain polymers (up to 20:6) no significant differences in polydispersity and absorption spectra were observed for polyenes prepared using the "batch" or the "stepwise" addition of the monomer mixture. However, longer copolyenes prepared by batch addition (e.g., FcC≡CH: TCDTF6 = 20:20) exhibited slightly lower molar extinction coefficients and blue-shifted absorption maxima compared to copolyenes prepared by stepwise addition. It is interesting to note that the retro Diels–Alder reaction, which usually requires temperatures of ~120 °C,[29,30] proceeds at significantly lower temperatures in the copolymers prepared here. In fact, any copolymer heated to 120 °C showed decreased solubility and the formation of high molecular weight compounds (as detected by GPC), both indicative of intramolecular and intermolecular side reactions involving the relatively electron-rich polyene chain. Side reactions did not take place over a period of 10 minutes when the retro Diels–Alder reaction was carried out at 70 °C. The UV/vis spectra of the copolyenes, in general, were significantly more intense and red-shifted (out to 800 nm with a maximum around 480 nm) compared to UV/vis spectra of poly(ethynylferrocene) itself. For example, the polymers whose spectra are shown in Figure 5 (top; ϵ = 87 000) and Figure 1 (top; ϵ = 52 000) both contain 60 double bonds. As a consequence of these polymers absorbing light at 690 nm, M_n had to be measured by viscometry rather than light scattering. Interestingly, the copolyenes are not especially air sensitive; a solution of (FcC≡CH)$_{20}$(TCDTF6)$_{20}$ in THF showed a decrease of only ~5% in the low energy absorption when exposed to air for a period of about 2 h.

Block copolymers prepared by adding 20 equiv of ethynylferrocene and (4 h later) 20 equiv of TCDTF6 were found to have a high polydispersity (>2) and a UV–vis spectrum similar to the ethynylferrocene homopolymers. No red shift in absorption or enhanced molar extinction coefficient was observed. However, it should be noted that the retro Diels–Alder reaction in the *block* copolymers probably would require temperatures in excess of 100 °C to form the unsubstituted polyene block, but the quality of samples heated to this temperature in fact degraded rather than improved. Therefore, we propose that the *copolymers* that contain an equal number of equivalents of ethynylferrocene and TCDTF6, after capping and heating to 70 °C, have a structure that *on the average* contains a ferrocene-substituted double bond followed by two unsubstituted double bonds, as shown in Scheme 3. The fact that

Table 4. Copolyenes Prepared from Mixtures of Ethynylferrocene and TCDTF6[a]

ratio	PDI	C=C no.	M_n(visc)[b]	M_n(calcd)	yield (%)	λ_{max} (ϵ)	solvent
10:2	1.63	14	2400	2422	40	470 (1.3×10^4)	toluene
10:4	1.36	18	2300	2518	40	474 (2.1×10^4)	THF
10:10[c]	1.47	30	4300	2674	90	470 (4.8×10^4)	THF
20:4	1.10	28	5300	4618	70	474 (4.6×10^4)	toluene
20:8	1.33	36	4200	4810	85	468 (3.8×10^4)	THF
20:20[c]	1.58[d]	60	6900	5122	96	490 (8.7×10^4)	THF
30:6	1.30	42	7700	6814	90	470 (7.1×10^4)	THF
30:30	1.70[d]	90	8100	7966	80	450 (5.1×10^4)	THF

[a] Ratio of ethynylferrocene to TCDTF6. Reaction time 24 h total. Capped with pyridinealdehyde (10 equiv) over a period of 24 h and heated to 70 °C for 10 minutes after capping. [b] Absorption at 690 nm prevented measurement of the molecular weight by light scattering. [c] Added in (5:5 equiv) portions 2 h apart (see the Experimental Section). [d] Incomplete elimination of 1,2-bis(trifluoromethyl)benzene.

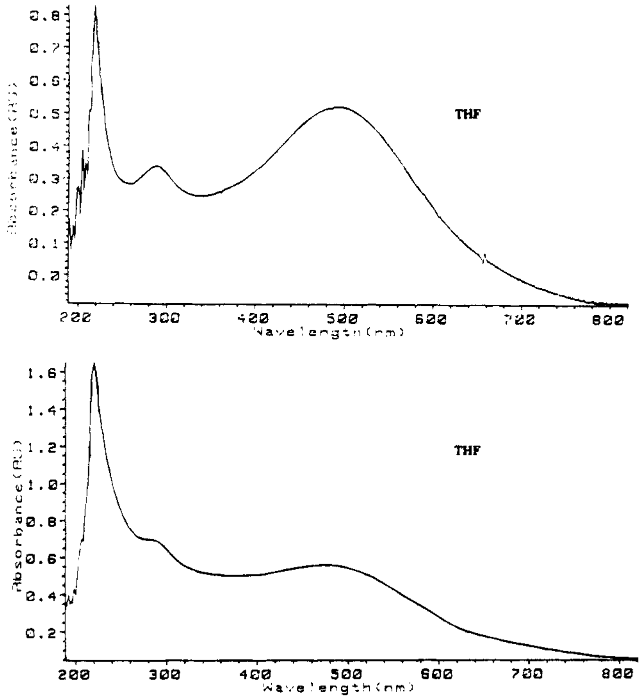
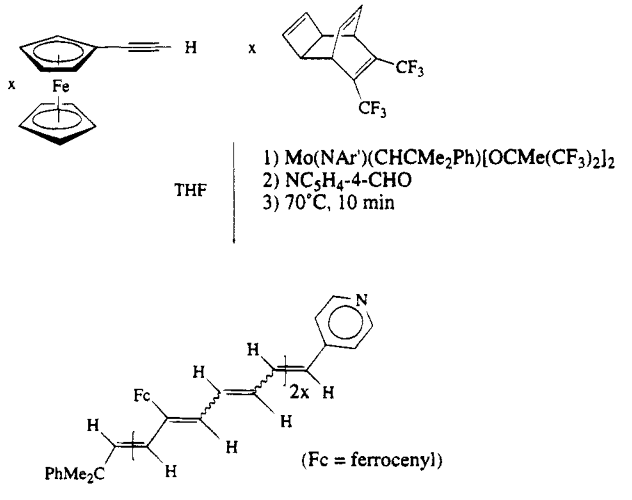


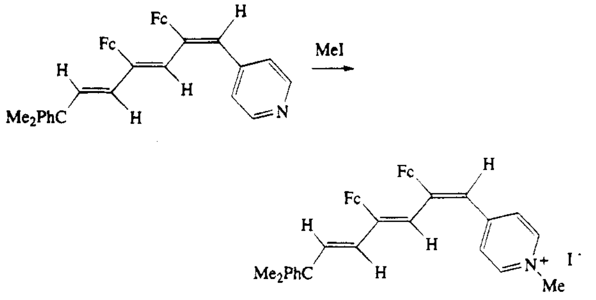
Figure 5. UV/vis spectra of copolyenes prepared from poly($FcC{\equiv}CH$)$_{20}$(TCDTF6)$_{20}$ (top) and poly($FcC{\equiv}CH$)$_{20}$(TCDTF6)$_4$ (bottom).

Scheme 3



there is no significant difference in the polydispersity or in the UV–vis spectra of *short*-chain polymers, no matter how the monomers are added (batch or stepwise addition), suggests that there is a tendency toward an alternating polymer structure.

Synthesis of Charged Polymers. Positively charged polymers were prepared by treating pyridine-4-carboxaldehyde-capped polymers with neat methyl iodide. The general applicability of this approach was proven by proton NMR and mass spec for the quaternized 2-mer. The quaternized 5-*trans*-1-(*N*-methylpyridinio-2,4-diferrocenyl-7,7-dimethyl-7-phenyl-1,3,5-heptatriene iodide exhibited a bathochromic shift (595 nm in $CHCl_3$) compared to the uncharged 5-*trans*-1-pyridyl-2,4-diferrocenyl-7,7-dimethyl-7-phenyl-1,3,5-heptatriene (464 nm in $CHCl_3$) (eq 3). (No reaction was observed under analogous conditions between methyl iodide and the analogous poly(ethynylferrocene) samples that had been capped with ferrocene carboxaldehyde.) These polymers could not be characterized by GPC methods as a consequence of their charged nature. Virtually identical polymers were obtained by terminating the living end with *N*-methylpyridinium-4-carboxaldehyde triflate or iodide. UV/vis absorption spectra of the quaternized polymers (Figure 6) showed a tailing of the absorption out to nearly 800 nm. Proton NMR spectra of the charged systems show no methyl groups in the region of 0–3 ppm, indicating that no internal chain alkylation had taken place and the *N*-methyl group could be observed at 3.7 ppm as a broad resonance.



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Other Initiators. Recently we showed that α insertion of *o*-TMS-substituted phenylacetylene could be encouraged through the use of initiators that contained small alkoxides such as Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(OC_6F_5)$_2$(quinuclidine) or Mo(NAd)($CHCMe_2Ph$)[$OCH(CF_3)_2$]$_2$(2,4-lutidine) (Ad = adamantyl).[19] Therefore, we were surprised to find that ethynylferrocene is *not* polymerized smoothly by these "small alkoxide" catalysts. Furthermore, examination by NMR showed that new H_α alkylidene resonances were observed (e.g., at 14.63, 14.41, 14.28, 14.21, 13.79, 13.68, and 13.42 ppm in the case of the pentafluorophenoxide initiator) that can be ascribed to sequential β insertions. No resonances characteristic of a trans double bond formed in an α insertion process were observed. We also found that although ethynylferrocene reacts with Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(O-t-Bu)$_2$ via α addition, the first insertion reaction is extremely slow, and the first insertion product does not react further to give polymer.

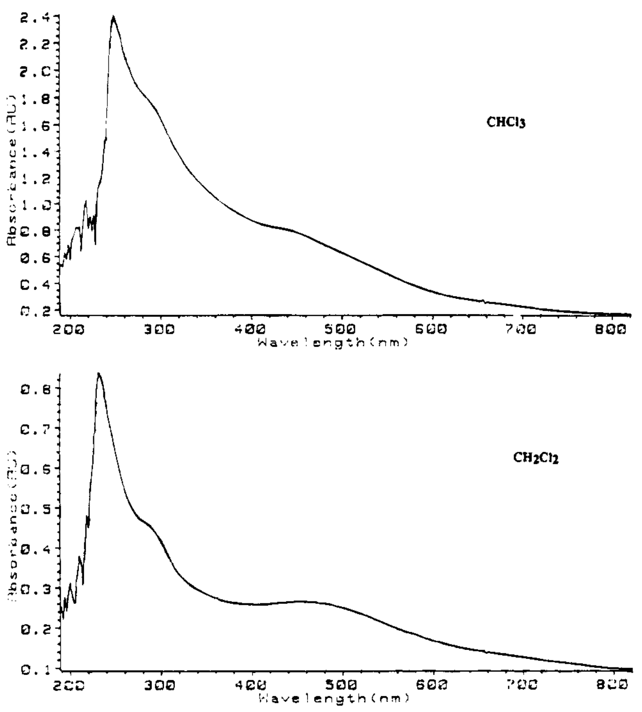

Figure 6. UV/vis spectra of quaternized polyenes poly$(FcC{\equiv}CH)_{30}PyMe^{+}]^{-}$ (top) and poly$(FcC{\equiv}CH)_{30}(TCDTF6)_{6}$-$PyMe^{+}]^{-}$ (bottom).

Discussion

The present hypothesis is that alkynes and olefins react with initiators of the type employed here at one of the CNO faces of the pseudotetrahedral $MoCNO_2$ core to give the initial metallacyclobutene or metallacyclobutane, respectively.[16,19] An especially sterically demanding terminal alkyne therefore would be encouraged to add to an alkylidene so as to yield the α-substituted metallacycle as a consequence of steric interaction between the alkyne substituent and the initial and propagating alkylidene(s) but to add to yield the β-substituted metallacycle as a consequence of steric interaction between the alkyne substituent and the imido and alkoxide ligands on the CNO face. Electronic factors would appear to favor α addition if the alkyne substituent were capable of stabilizing the negative charge on an α carbon atom of a metallacycle and β addition if the alkyne substituent were capable of stabilizing a positive charge, although electronic preferences of this sort are virtually unexplored. The fact that ethynylferrocene adds solely α to the $OCMe(CF_3)_2$ initiator and to the propagating alkylidene(s) therefore could be ascribed to repulsion between the ferrocenyl substituent on the incoming alkyne and alkylidene ligands. The fact that it adds β to initiators that contain "small" alkoxides (OC_6F_5 or $OCH(CF_3)_2$) that in fact were developed in order to *encourage* α addition[19] therefore is a surprising result that we still cannot explain. It should be noted, however, that mechanistic investigations for a variety of catalysts of the general type employed here are ongoing and many details are still unclear. It is even still possible, for example, that monomer attack on a CNO face is not universal, i.e., that attack on the COO face of the catalyst might be possible in some circumstances.

The homopolymers obtained from ethynylferrocene and ethynylruthenocene clearly are not highly conjugated, presumably for steric reasons, even though they are head-to-tail polymers. Therefore, the homopolymers having a single charge at the end of the chain are similar to the uncharged homopolymers, at least in terms of UV/vis spectra; the charge is simply localized near one end of the chain, and most of the UV/vis absorption spectra can be ascribed to the long, relatively poorly conjugated uncharged polymer chains.

The ability to synthesize copolyenes from copolymers of ethynylferrocene and TCDTF6 was unexpected, even though we had already demonstrated that the $OCMe(CF_3)_2$ catalyst would polymerize TCDTF6 in a controlled manner.[18] We were especially surprised to find that the copolyenes tended toward alternation. In fact, it is not out of the question that a relatively electron-rich, but sterically bulky disubstituted alkylidene would react most readily with TCDTF6 and that the deactivated primary alkylidene derived from TCDTF6 would react most rapidly with the relatively electron-rich ethynylferrocene and therefore that TCDTF6 and ethynylferrocene would thus be incorporated alternately in the growing polymer chain. The dramatic increase in conjugation in the case of 1:1 copolymers suggests that few if any 1,3-interactions exist in the copolyenes and that on the average one ferrocene is found on every sixth olefinic carbon atom. Since 1:1 copolyenes possess at least two unprotected double bonds in sequence and are relatively electron rich, it is surprising that the polyenes are not more sensitive to oxidation by air.

These copolyenes or "functionalized polyacetylenes" described here should be compared with those prepared by the ring-opening metathesis of monosubstituted cyclooctatetraenes with similar catalysts.[31-33] Unfortunately, ring opening of cyclooctatetraenes does not give rise to low-PDI polyenes. Also a single substituent on the polyacetylene chain per every eight carbon atoms on the average also apparently is not sufficient to prevent aggregation and/or cross-linking of these polyenes; i.e., as many as six sequential unsubstituted double bonds could be present in a given chain. In the copolyenes that we have prepared here, the use of less than 50% TCDTF6 reduces the possibility that long unsubstituted polyene sequences will be present. However, if significantly less than 50% TCDTF6 is employed, then steric interaction between neighboring ethynylferrocene units leads to a lower degree of conjugation.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless stated otherwise. Pentane was washed with sulfuric/nitric acid (95/5, v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent-grade diethyl ether, tetrahydrofuran, toluene, and benzene were distilled from sodium benzophenone ketyl under nitrogen. Reagent-grade dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina prior to use. Pyridine-4-carboxaldehyde as well as methyl iodide were degassed under high vacuum and dried over molecular sieves (3 Å). Ferrocenecarboxaldehyde was purchased commercially and used as received. Ethynylferrocene,[34] ethynylruthenocene,[35] and TCDTF6[29] (7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene) were synthesized as described in the literature. *N*-Methylpyridinium-4-carboxaldehyde iodide and *p*-trimethylammoniumbenzaldehyde iodide were prepared by adding methyl iodide to a solution of the pyridine in ether, followed by extensive washing of the precipitate with diethyl ether. Pyridinium-4-carboxaldehyde triflate was similarly prepared from pyridine-4-carboxaldehyde and methyl triflate.

NMR data were recorded at 300 MHz unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hertz. Spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. GPC data were determined on a Spectroflow 400 using a Mini Dawn light scattering detector (Wyatt Technologies) and a Viscotek differential refractometer, respectively (flow rate 1 mL/min). Shodex KF-802.5, 803, 804, 805, and 800P columns were used. UV data were obtained on a HP 8452A UV detector (range 190−820 nm) in the solvent indicated and are listed in nanometers. Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)($OR)_2$ (R = t-Bu, hexafluoro-*tert*-butyl,[26] OC_6F_5[19]) and Mo(NAd)($CHCMe_2Ph$)-[$OCH(CF_3)_2]_2$[19] were prepared as described in the literature. Benzene and toluene used for polymerizations were stored over Na/K alloy. All polymerization solvents were passed over dry alumina prior to use.

Isolation of the Ferrocenecarboxaldehyde-Capped First Insertion Product. Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)-[$OCMe(CF_3)_2]_2$ (16 mg, 22.6 μmol) was dissolved in 1 mL of toluene, and a solution of ethynylferrocene (6 mg, 28.6 μmol) in 4 mL of toluene was added. The reaction mixture was stirred for 2.5 h. No new alkylidene H_α resonances were observed. A solution of ferrocenealdehyde (15 mg, 70 μmol) was added, and the mixture was stirred overnight. The mixture was passed over a column of silica gel (220−440 mesh, 4 × 70 cm, made up in *n*-hexane:diethyl ether = 50:50). The product (2-*trans*-1,2-diferrocenyl-5-methyl-5-phenylhexa-1,3-diene) eluted as the first orange band and was recrystallized from a mixture of ether and pentane: yield 10 mg (0.019 mmol, 65%); ^{1}H NMR ($CDCl_3$) δ 7.24 (d, 2, J = 8, H_o), 7.18 (t, 1, J = 8, H_p), 7.11 (t, 2, J = 8, H_m), 6.51 (s, 1, C*H*), 6.44 (d, 1, J = 16.2, CHC*H*CMe$_2$Ph), 6.11 (d, 1, J = 16.2, C*H*CHCMe$_2$Ph), 4.42 (t, 2, J = 2.4, Cp′), 4.40 (t, 2, J = 2.4, Cp′), 4.27 (t, 2, J = 2.4, Cp′), 4.23 (t, 2, J = 2.4, Cp′), 4.13 (s, 5, Cp), 4.12 (s, 5, Cp), 1.23 (s, 6, Me); ^{13}C NMR ($CDCl_3$) δ 148.6, 138.3, 137.5, 122.1, 126.7, 126.3, 125.8, 125.5, 123.2, 86.8 (C_{ipso}), 69.0 (Cp), 68.9 (Cp), 68.3 (Cp′), 68.0 (Cp′), 67.3 (Cp′), 66.3 (Cp′), 28.0 (Me); LRMS (EI, 70 eV), found for $C_{33}H_{32}Fe_2$ 540 (M^+); UV (THF) 234, 280, 450 nm.

Isolation of the Ferrocenecarboxaldehyde-Capped Second Insertion Product. The compound was synthesized and isolated following the procedure described above, using 34 mg (48 μmol) of the initiator, 20 mg (95 μmol) of ethynylferrocene in 15 mL of toluene, and 40 mg of ferrocenaldehyde (0.19 mmol). The product was recrystallized from a mixture of diethyl ether and pentane (17 mg, 0.023 mmol, 36%): ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 2, H_o), 7.19 (d, 1, J = 8, H_p), 7.11 (d, 2, J = 8, H_m), 6.53 (s, 1, C*H*), 6.51 (s, 1, C*H*), 6.43 (d, 1, J = 18, CHC*H*CMe$_2$Ph), 6.11 (d, 1, J = 18, C*H*CHCMe$_2$Ph), 4.71 (t, 2, J = 1.8, Cp′), 4.46 (t, 2, J = 1.8, Cp′), 4.44 (t, 2, J = 1.8, Cp′), 4.40 (t, 2, J = 1.8, Cp′), 4.34 (t, 2, J = 1.8, Cp′), 4.28 (t, 2, J = 1.8, Cp′), 4.23 (s, 5, Cp), 4.13 (s, 5, Cp), 4.08 (s, 5, Cp), 1.23 (s, 6, Me); ^{13}C NMR ($CDCl_3$) δ 148.8 142.5, 136.3, 128.0, 126.3, 125.6, 125.5, 123.8, 122.9, 88.0 (C_{ipso}), 87.5, 83.5 (C_{ipso}), 69.5 (Cp), 69.3 (Cp), 69.25 (Cp), 69.1 (Cp′), 68.7 (Cp′), 68.5 (Cp′), 68.2 (Cp′), 67.5 (Cp′), 66.6 (Cp′), 28.2 (Me); LRMS (EI, 70 eV), found for $C_{45}H_{42}Fe_3$ 750 (M^+, 50%), 631 (M^+ − Me_2CPh; 100%), 446 (M^+ − ferrocenyl − Me_2CPh, 29%).

Isolation of the Pyridine-4-carboxaldehyde-Capped Second Insertion Product. 5-*trans*-1-Pyridinyl-2,4-diferrocenyl-7,7-dimethyl-7-phenyl-1,3,5-heptatriene was synthesized following the procedure described above, using 16 mg (22.6 μmol) of initiator, 10 mg (48 μmol) of ethynylferrocene in 15 mL of toluene, and 10 mg of pyridinecarboxaldehyde (93 μmol). The product was recrystallized from a mixture of diethyl ether and pentane; yield 5 mg (7.8 μmol, 33%); ^{1}H NMR ($CDCl_3$) δ 8.48 (d, 2, J = 7, H_o), 7.35 (d, 2, J = 7, H_m), 7.19 (d, 2, J = 6, H_o), 7.11 (t, 1, J = 6, H_p), 7.00 (d, 2, J = 8, H_m), 6.69 (s, 1, C*H*), 6.63 (s, 1, C*H*), 6.66 (d, 1, J = 16, CHC*H*CMe$_2$Ph), 6.44 (d, 1, J = 16, C*H*CHCMe$_2$Ph), 4.47 (t, 2, J = 1.8, Cp′), 4.41 (t, 2, J = 1.8, Cp′), 4.32 (t, 2, J = 1.8, Cp′), 4.30 (t, 2, J = 1.8, Cp′), 4.16 (s, 5, Cp), 4.11 (s, 5, Cp), 1,17 (s, 6, Me); ^{13}C NMR ($CDCl_3$) δ 149.6 (C_o), 148.2 (C_{ipso}), 144.5 (C_m), 128.1, 126.0, 125.8, 123.4, 123.0, 122.9, 122.1, 86.3 (C_{quat}), 69.5 (Cp), 69.1 (Cp), 68.6 (Cp′), 67.4 (Cp′), 67.5 (Cp′), 12.5 (Me); LRMS (EI, 70 eV), found for $C_{40}H_{37}Fe_2N$ 643 (M^+, 11%), 524 (M^+ − Me_2CPh, 100%), 339 (M^+ − ferrocenyl − Me_2CPh, 36%); UV (THF) 238, 280, 475; UV ($CHCl_3$) 258, 300, 464.

Quaternization of the Pyridine-Capped Second Insertion Product. 5-*trans*-1-Pyridinyl-2,4-diferrocenyl-7,7-dimethyl-7-phenyl-1,3,5-heptatriene (15 mg, 23.3 μmol) was dissolved in 20 mL of diethyl ether, and methyl iodide (1 mL, 3.1 mmol) was added. The solution was stirred overnight. The solvent was decanted from the black precipitate, and the residue was recrystallized from a mixture of THF and diethyl ether; yield 14 mg (17.8 μmol, 78%): ^{1}H NMR ($CDCl_3$) δ 8.58 (d, 2, J = 6.3, H_o), 7.75 (d, 2, J = 6.3, H_m), 7.2 (m, 3, H_{o+p}), 7.08 (d, 2, J = 8.4, H_m), 6.74 (s, 1, C*H*), 6.65 (s, 1, C*H*), 6.40 (d, 1, J = 16.2, CHC*H*CMe$_2$Ph), 5.95 (d, 1, J = 16.2, C*H*CHCMe$_2$Ph), 4.60 (t, 2, J = 1.8, Cp′), 4.57 (t, 2, J = 1.8, Cp′), 4.46 (t, 2, J = 1.8, Cp′), 4.41 (J = 2, J = 1.8, Cp′), 4.32 (s, 3, N*Me*), 4.21 (s, 5, Cp), 4.19 (s, 5, Cp), 1.21 (s, 6, Me); ^{13}C NMR ($CDCl_3$) δ 144.0, 128.3, 126.1, 125.9, 125.0, 121.3, 83.9 (C_{ipso}), 71.8 (Cp′), 70.5 (Cp), 69.7 (Cp′), 69.4 (Cp), 68.1 (Cp′), 65.9 (Cp′), 40.8 (Me), 15.3 (Me); LRMS (EI, 70 eV), found for $C_{41}H_{40}Fe_2N$ 658 (M^+, 1.2%), 643 ($M^{\bullet +}$ − CH_3, 11%), 524 ($M^{\bullet +}$ − CH_3 − Me_2CPh, 100%), 458 (M^+ − CH_3 − Me_2CPh − CpH, 54%), 401 (M^+ − CH_3 − Me_2CPh − CpH − Fe, 16%), 338 (M^+ − CH_3 − Me_2CPh − CpH − Fe − Cp, 42%); UV (THF) 340, 400 (sh), 548; UV ($CHCl_3$) 380, 412, 595.

Preparation of the Homopolymers. The initiator was dissolved in 10.0 mL of solvent, and a solution of the monomer (ethynylferrocene or ethynylruthenocene) in 5 mL of solvent was added at room temperature. The reaction mixture was stirred for the time indicated in the tables. A 10-fold excess of the aldehyde in 5 mL of solvent was added, and the solution was stirred for an additional 24 h. The polymer was precipitated by pouring the reaction mixture into pentane (20 mL). The precipitate was washed with pentane until the washings were colorless and dried in vacuo.

Preparation of Copolymers. **(a)** The catalyst was dissolved in 10.0 mL of solvent, and a solution of ethynylferrocene and TCDTF6 in 5 mL of solvent was added at room temperature. The reaction mixture was stirred for the time indicated in the tables. A 10-fold excess of the capping aldehyde in 5 mL of solvent was added, and the solution was stirred for an additional 24 h. After heating the mixture to 70 °C for 10 min, the polymer was precipitated by pouring it into pentane (20 mL). The precipitate was washed with pentane until the washings were colorless and dried in vacuo.

(b) As described in a, except the mixture of monomers was added in equal 5 equiv portions every 2 h. Therefore, for the 10:10-mer two portions of a 5:5 mixture were added, for a 20: 20-mer four portions of a 5:5 mixture, etc.

Quaternization of Pyridine-Capped Polymers. The polymers were suspended in a mixture of THF and MeI (70: 30) or neat MeI and stirred for 24 h. The solvents were removed in vacuo.

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