Vinyl Reactivity of (η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten, a Novel Organometallic Monomer

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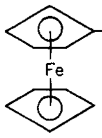
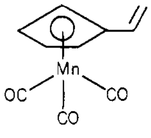
ABSTRACT: The first vinyl organometallic monomer containing tungsten, (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (4), was homopolymerized and copolymerized with styrene, acrylonitrile, methyl methacrylate, and *N*-vinyl-2-pyrrolidone, using azobis(isobutyronitrile) (AIBN) as the initiator. Reactivity ratios for the styrene (M_2) copolymerization of 4, initiated by AIBN in benzene solutions, were $r_1 = 0.16$ and $r_2 = 1.55$ from which the Alfrey–Price parameters $e = -1.98$ and $Q = 1.66$ were calculated. Thus, (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten is an exceptionally electron-rich vinyl monomer, closely resembling vinylferrocene, (η^5-vinylcyclopentadienyl)tricarbonylmanganese, and (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium in this respect. This is the first vinyl monomer known to have an M–CH_3 (M is a transition metal) bond. Styrene polymerizations in the presence of (η^5-cyclopentadienyl)tricarbonylmethyltungsten were carried out to evaluate the possibility that the methyl group is a good hydrogen atom donor (thereby serving as an inhibitor or a chain transfer agent). No evidence was obtained for significant chain transfer activity. Similarly, neither (η^5-cyclopentadienyl)tricarbonylmanganese nor poly(η^5-vinylcyclopentadienyl)tricarbonylmanganese acted as efficient chain transfer agents in styrene polymerizations.

Interest in organometallic polymers is currently rising in view of their potential use as catalysts, semiconductors, UV absorbers, and lithographic resists among others.[2] Since the first radical-initiated polymerization of vinylferrocene by Arimoto and Haven[3] in 1951, other vinyl monomers containing transition metals have been prepared and polymerized.[4,5] Representative examples include (η^6-styrene)tricarbonylchromium,[6] (η^5-vinylcyclopentadienyl)tricarbonylmanganese,[7,8] vinylferrocene,[9] (η^6-benzyl acrylate)tricarbonylchromium,[10] ferrocenylmethyl acrylate,[11,12] and (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium.[13,14] Anionic initiation[15] has also been examined for some of these monomers.

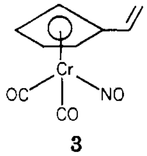
Not much is known about the effect of organometallic moieties on the polymerization behavior of vinyl groups. Vinylferrocene (1), (η^5-vinylcyclopentadienyl)tricarbonylmanganese (2), and (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (3) are now known, from the application of the Alfrey–Price *Q*–*e* scheme to their copolymerizations, to possess very electron-rich vinyl groups. The AIBN-initiated homopolymerization of 2 in benzene, benzonitrile, and acetone followed[16] the rate expression $V_p = k[M]^{1.5}[I]^{0.5}$. The 1.5 order in monomer concentration was the result of low initiator efficiency where $k_i \propto [M]$ and this was substantiated[16] by demonstrating that the degree of polymerization, $\overline{DP}$, was proportional to $([M]/[I])^{0.5}$. Alternately, vinylferrocene (1) undergoes a novel unimolecular termination reaction when homopolymerized in benzene.[17]



1
$e = -2.1$



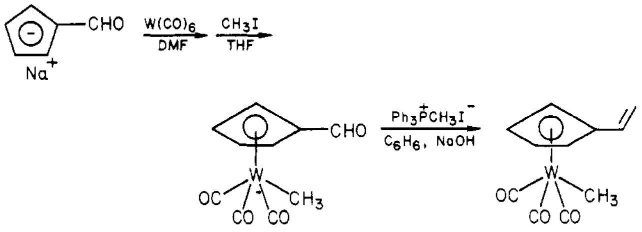
2
$e = -1.99$



3
$e = -1.98$

Since studies of (vinylcyclopentadienyl)metal carbonyls are so rare (confined to 1–3), our synthesis of (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (4) (Scheme I) was of interest because it represented the first organotungsten vinyl monomer to be prepared. Furthermore, it contains the unique metal–carbon σ bond where a methyl group is directly attached to tungsten. The effect of the tungsten on the adjacent α hydrogens is unknown and the question of whether that methyl group will serve as a good hydrogen atom donor, thereby acting as a polymerization inhibitor, or as a chain transfer site, arises. Furthermore, monomers 1–3 all possess first-row transition metals bound to a cyclopentadienyl ring. Conversely, monomer 4 contains a third-row transition metal and this may modify electronic effects as well as steric effects at the vinyl group.

Scheme I



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Results and Discussion

Reviews of the addition polymerization of vinylorganometallic monomers[4,5,18] reveal that the (η^5-vinylcyclopentadienyl)metal monomers 1–3 are exceptionally electron rich, exhibiting Alfrey–Price *e* values[19,20] of −2.1, −1.99, and −1.98, respectively. This can be put into perspective by noting that for 1,1-dianisylethylene $e = -1.96$.[20] In searching for a candidate third-row transition-metal η^5-vinylcyclopentadienyl monomer for polymerization reactivity studies, we noted that (η^5-cyclopentadienyl)tricarbonylmethyltungsten (5), first prepared by Fischer in 1955,[21] was stable to air and moisture.[22] However, its vinyl derivative, 4, had never been prepared. The recent facile synthesis of the formylcyclopentadienide salt of sodium and its reactivity with metal carbonyls[23] suggested (5) the route outlined in Scheme I would be viable. Indeed, treating this salt with hexacarbonyltungsten in refluxing

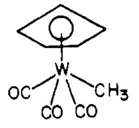

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Table I
Homo- and Copolymerization of 4 (M_1) in Benzene at 60 °C

no.	copolymer desig[a]	M_1 in feed, mol	M_1 in feed, mol %	AIBN, mol	C_6H_6, mL	time, h	copolymer yield, %	copolymer % C	copolymer % W	M_1 in copolymer, mol %	$[\eta]_{THF}$[30]
1	PVCT	1.3×10^{-3}	100	4.1×10^{-5}	3	158	12				
2	PVCT[b]	1.6×10^{-3}	100	6.5×10^{-5}	3	48	33	35.3	49.2	100	0.31
3	P(VCT-AN)	1.3×10^{-3}	30	1.4×10^{-4}	3	158	65	39.8	37.9	32	0.28
4	P(VCT-MMA)	1.4×10^{-3}	30	1.4×10^{-4}	3	158	77	45.6	26.0	23	0.30
5	P(VCT-NVP)	1.3×10^{-3}	30	1.5×10^{-4}	3	158	52	40.0	36.9	47	0.32
6	P(VCT-ST)[b]	2.4×10^{-3}	90	6.5×10^{-5}	5	4	29	40.1	45.0	75	0.33
7	P(VCT-ST)[c]	5.5×10^{-4}	3.2	3.9×10^{-6}	2	60	9	86.9	4.0	2.4	
8	P(VCT-ST)[b]	1.6×10^{-3}	30	1.2×10^{-4}	4	30	32	44.7	31.6	34	
9	P(VCT-ST)[b]	2.0×10^{-3}	47	1.3×10^{-4}	4	37	58	53.1	30.3	31	

[a] VCT = 4, ST = styrene, AN = acrylonitrile, MMA = methyl methacrylate, NVP = *N*-vinyl-2-pyrrolidone, AIBN = azobis(isobutyronitrile). [b] Polymerization followed by GC; reinitiated three times; final yields are given. [c] Run at 50 °C.

DMF followed by removal of DMF, addition of THF, and treatment with methyl iodide gave (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten in 82% yield after purification by chromatography and sublimation.[24] Monomer 4 was prepared from the aldehyde by using triphenylmethylphosphonium iodide, aqueous 5 N NaOH, and benzene under phase-transfer conditions.[24,25] Monomer 4 was obtained as bright yellow crystals which could be sublimed and was identical with an authentic sample.[24]

Polymerization Studies. Radical Initiation. Homopolymerization of 4 was accomplished in benzene, using AIBN initiation at 60 °C. The yields could be increased by multiple initiation. A 0.5 M solution of 4 gave a 33% homopolymer yield ($[\eta]_{THF}$[30] 0.31 dL/g) in 48 h, using three reinitiations with AIBN. Copolymerizations of 4 and styrene in benzene were also sluggish, giving low yields unless the reaction was reinitiated several times. A 75% yield of styrene copolymer could be obtained after four reinitiations. Copolymers were also obtained with *N*-vinyl-2-pyrrolidone, methyl methacrylate, and acrylonitrile. They are summarized in Table I, and Scheme II lists key infrared stretching frequencies. The rather low intrinsic viscosities of the copolymers and the slow homo- and copolymerization rates suggested the following: (1) monomer 4 may initiate with poor efficiency; (2) monomer 4 may have a steric retardation of its propagation; (3) the tungsten-bound methyl group may either inhibit polymerization or serve as a chain transfer site.

The reactivity ratios were obtained in a series of 4/styrene copolymerizations. Styrene (M_2) was chosen because it is moderately electron rich ($e = -0.80$). Since we anticipated 4, like 1–3, might be electron rich, the choice of an electron-rich comonomer would avoid any complexities caused by charge-transfer complex formation. Furthermore, styrene had been used previously in r_1, r_2, and Q–e studies with monomers 1–3.[18] The disappearance of the monomers was followed by GLC so that the incorporation of M_1 and M_2 into the copolymer could be determined at several conversions for each individual copolymerization. Several different $[M_1]_0/[M_2]_0$ ratios were employed and all the data points were analyzed by a nonlinear least-squares fitting program[26] for the integrated form of the copolymer equation which employed the methods described by Tidwell and Mortimer.[26,27] In addition to using the nonlinear fitting technique, $[M_1]_0/[M_2]_0$ ratios were chosen in the vicinity of the "optimized values" for use in the r_1, r_2 calculations.[27,28] The composition–conversion data for styrene copolymerizations are shown in Table II, from which $r_1 = 0.16$ (0.135–0.183) and $r_2 = 1.55$ (1.41–1.71). The 95% joint confidence limits are plotted in Figure 1. The small value of r_1 and large value of r_2 show the same pattern exhibited by monomers 1–3 in styrene copolymerizations.

Table II
Composition–Conversion Data for Copolymerization of (η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten (M_1) with Styrene (M_2)[a]

run	M_1 in feed, mol %	conversion, %	M_1 in copolymer, mol %
1	3.20	9.03	2.4
2	21.50	7.40	15.0
3a	29.90	10.27	20.8
3b	29.90	11.87	18.2
3c	29.90	19.10	20.9
3d	29.90	30.30	22.2
4	46.19	25.37	27.3
5a	49.41	16.20	32.9
5b	49.41	22.10	36.4
5c	49.41	22.20	34.5
5d	49.41	28.18	32.8
6a	71.41	5.17	45.3
6b	71.41	9.88	47.9
6c	71.41	18.42	40.1
7a	90.90	3.34	71.5
7b	90.90	19.79	76.1
7c	90.90	23.13	76.3
7d	90.90	28.70	79.9

[a] From these data the calculated reactivity ratios for this monomer pair are $r_1 = 0.16$ and $r_2 = 1.55$.

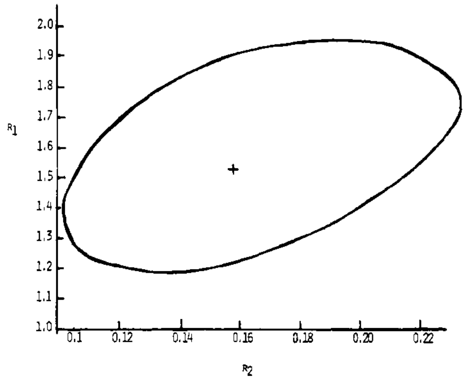


Figure 1.

The values of Q and e were calculated from the reactivity ratios using

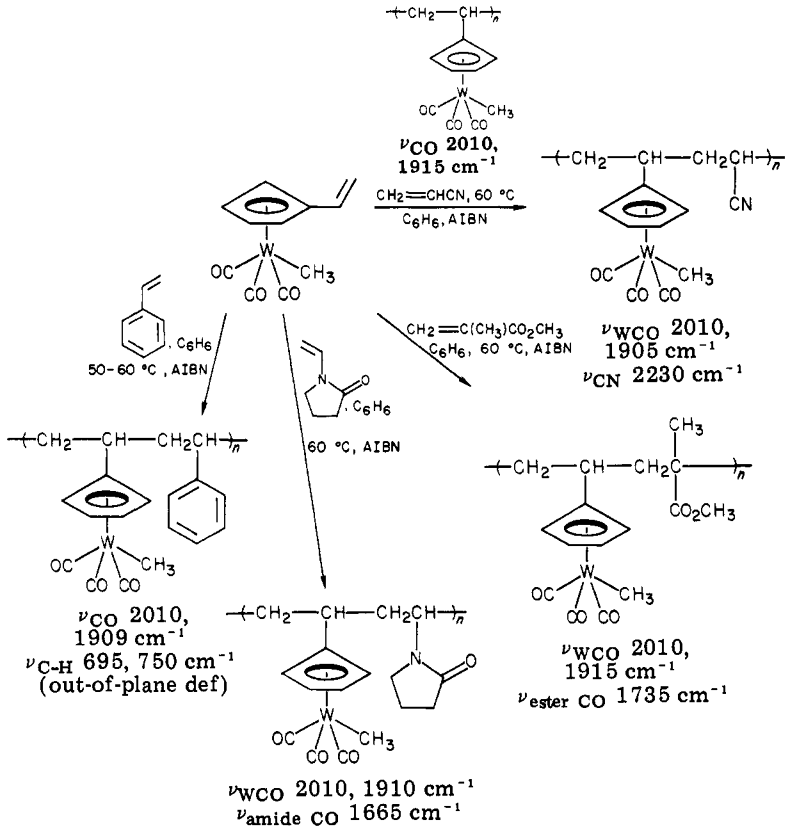
$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)]$$

$$r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)]$$

$$r_1 r_2 = \exp[-(e_1 - e_2)^2]$$

and $Q_2 = 1.0$ and $e_2 = -0.80$ for styrene (M_2).[20] Monomer

Scheme II



4 proved to have an exceptionally electron-rich vinyl group according to its large value of e (−1.98). Thus, 4 appears to be almost identical with, in this respect, its related iron, manganese, and chromium monomers 1–3. All of these have considerably more electron-rich vinyl groups than 2-vinylthiophene (e = −0.80), suggesting the π orbitals of the cyclopentadienyl ring of 1–4 resemble those of the cyclopentadienyl anion. The resonance parameter Q is 1.66 for 4. This value may be compared with the values of Q for p-methoxystyrene (1.36), p-nitrostyrene (1.63), 2-vinylthiophene (2.86), and monomer 3 (3.1). The high value of Q suggests a strong resonance interaction between the radical center and the cyclopentadienyl ring of 4, but the role of the $W(CO)_3CH_3$ group cannot be ascertained. One might expect that unpaired spin density is mainly concentrated on the carbon skeleton based on previous generalizations that spin density is mainly found on the carbon framework while most charge density perturbations are found on the metal in organometallic radicals and cations.

The Q–e values of 4 and several other monomers are summarized in Table III. In addition, the Q–e scheme has been used to predict the relative reactivity ratios between these other monomers and 4. These predictions are tabulated in Table III.

Table III
Predicted Values of r_1 and r_2 in Copolymerizations of Monomer 4 (M_1) with Other Monomers Calculated from the Experimental Values of Q_1 and e_1 and the Literature Values for Q_2 and e_2 [a]

			calcd	
M_2	Q_2	e_2	r_1	r_2
1	1.08	−2.10	1.93	0.51
2	1.03	−1.99	1.59	0.63
3	3.13	−1.98	0.52	1.91
N-vinyl-2-pyrrolidone	0.14	−1.14	2.21	0.22
vinyl chloride	0.024	0.20	0.90	0.01
methyl methacrylate	0.74	0.40	0.02	0.17
acrylonitrile	0.44	1.20	0.007	0.006

[a] The values Q_1 = 1.66 and e_1 = −1.98 for 4 (M_1) were employed.

Table IV
Chain Transfer Experiments with (η^5-Cyclopentadienyl)tricarbonylmethyltungsten (5) in Styrene Polymerizations[a]

no.	[Sty], mol·L^{-1}	[5], mol·L^{-1}	[5]/[Sty] × 10^2	R_p × 10^6 mol·L^{-1}·s^{-1}	$\overline{M}_\eta$ × 10^{-3}
1	1.61	0.054	3.35	4.95	16.4
2	1.61	0.082	5.09	5.81	17.4
3	1.61	0.100	6.21	5.45	17.7
4	1.64	0.123	7.50	5.21	16.8
5	1.56	0.244	15.64	5.77	18.8
6	1.62	none		5.97	19.2

[a] Homopolymerizations of styrene were initiated by AIBN in benzene at 60 °C with (η^5-cyclopentadienyl)tricarbonylmethyltungsten as the possible chain transfer agent. [AIBN]/[Sty] was held constant at 1.017 × 10^{-2}. All experiments used 5 mL of benzene.

The low homo- and copolymerization rates and the low copolymer molecular weights suggested the methyl group of 4 might be exerting an inhibiting or chain transfer effect via hydrogen atom donation. To evaluate this possibility, we carried out styrene polymerizations in the presence of various concentrations of 5. Compound 5 is a perfect model for 4 because it cannot, itself, enter into a copolymerization with styrene. If the methyl group acted as a chain transfer site, this would depress the molecular weights of the polystyrene produced. The molecular weights of the polystyrene samples did not, however, vary appreciably with the addition of various concentrations of 5 (using AIBN initiation in benzene at 60 °C). These results are summarized in Table IV. Thus, hydrogen atom

Table V
Chain Transfer Experiments with (η^5-Cyclopentadienyl)tricarbonylmanganese (6) in Styrene Polymerizations[a]

no.	[Sty], mol·L^{-1}	[6], mol·L^{-1}	[6]/[Sty] × 10^2	R_p × 10^6, mol·L^{-1}	$\overline{M}_\eta$ × 10^{-3}
1	1.64	0.059	3.57	9.25	14.4
2	1.65	0.089	5.40	11.13	15.4
3	1.63	0.136	8.34	9.50	20.1
4	1.63	0.270	16.50	6.79	21.2
5	1.63	0.405	24.80	6.99	17.6
6	1.63			9.60	16.9

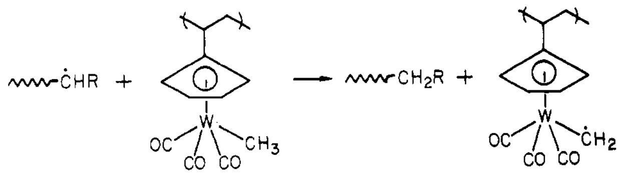
[a] Homopolymerizations of styrene were initiated by AIBN in benzene at 60 °C with 6 as the possible chain transfer agent. [AIBN]/[Sty] was held constant at 1.015 × 10^{-2}. All experiments used 5 mL of benzene.

Table VI
Chain Transfer Experiments with Poly(η^5-vinylcyclopentadienyl)tricarbonylmanganese (8) in Styrene Polymerizations[a]

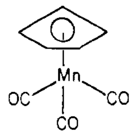
no.	[Sty], mol·L^{-1}	[8], g	R_p × 10^6, mol·L^{-1}·s^{-1}	$\overline{M}_\eta$ × 10^{-3}
1	9.59 × 10^{-3}	0.04	4.5	12.5
2	9.59 × 10^{-3}	0.012	4.5	14.5
3	9.59 × 10^{-3}		5.1	14.4

[a] Homopolymerizations of styrene were initiated by AIBN in benzene at 60 °C with 8 as the possible chain transfer agent. [AIBN]/[Sty] was held constant 9.89 × 10^{-2}.

abstraction by the growing chain from the tungsten-bound methyl group is not an important process.



A similar set of experiments was done with (η^5-cyclopentadienyl)tricarbonylmanganese (6) as a potential chain transfer agent. In this case, only the ring hydrogens would be available for abstraction. As shown in Table V, no decrease in polystyrene molecular weight occurred as the concentration of 6 was increased.



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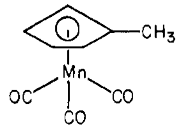
Again, this shows that no appreciable chain transfer activity is associated with the organometallic moiety. It is well-known that (η^5-methylcyclopentadienyl)tricarbonylmanganese (7) improves the octane number of gasoline. Apparently the ring methyl group donates hydrogen atoms to various radical species during combustion. Since each of the monomers 1–4 polymerize to give polymers with similar benzylic-like hydrogens along the backbone, chain transfer at this site may be important. Thus, styrene polymerizations were conducted in the presence of various concentrations of poly(η^5-vinylcyclopentadienyl)tricarbonylmanganese (8), which is an excellent polymer model (without the WCH$_3$ group) for polymers of 4. The results, shown in Table VI, prove that this polymer does not act as an efficient chain transfer agent because no marked change in polystyrene molecular weight occurs.



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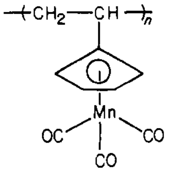

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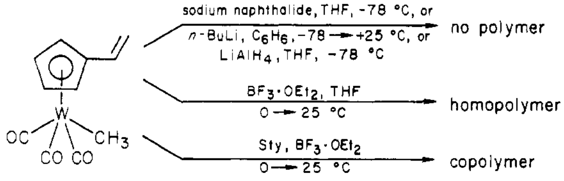
Anionic and Cationic Polymerization. The large negative value of e suggests that 4 should undergo cationic initiation and resist anionic initiation. Therefore anionic initiation was attempted by using (1) sodium naphthalide in THF at −78 °C, (2) n-butyllithium in benzene at −78 °C, initially followed by warming to ambient temperature over a 5-h period, and (3) $LiAlH_4$ in THF at −78 °C. Monomer to initiator ratios of 127–134 were used. No polymer was obtained in these anionic systems, in agreement with the large negative value of e.

An unsuccessful attempt to homopolymerize 4 was made using $BF_3·OEt_2$ in THF at an M/I ratio of 134. However, an identical reaction, initiated at 0 °C (2 h) and raised to ambient temperature overnight, resulted in a 4% yield of homopolymer. Thus cationic polymerization could be effected. The copolymerization of an equimolar solution of 4 (M_1) and styrene in THF, at an M/I ratio of 134, when initiated by $BF_3·OEt_2$ (at 0 °C for 2 h and raised to ambient temperature overnight) gave a 7% yield of copolymer (M_1/M_2 = 38/62). Both anionic and cationic initiation results are summarized in Table VII.



Experimental Section

All operations were done under nitrogen, using Schlenk tube techniques. Styrene was washed with aqueous 10% sodium hydroxide and 10% sulfuric acid to remove inhibitors, followed by distilled water washes, and it was then distilled over CaH_2 under

Table VII
Anionic and Cationic Polymerizations of Monomer 4[a]

no.	10[4], mol·L^{-1}	initiator	[initiator], mol·L^{-1}	solvent	temp, °C	polymer yield, %
1	2.68	sodium naphthalide	2.0 × 10^{-3}	THF	−78 → 25	0
2	2.68	n-BuLi	2.1 × 10^{-3}	benzene	−78 → 25	0
3	2.68	$LiAlH_4$	2.0 × 10^{-3}	THF	−78 → 25	0
4	2.69	$BF_3·OEt_2$	2.0 × 10^{-3}	THF	−78	0
5	2.68	$BF_3·OEt_2$	2.0 × 10^{-3}	THF	0 → 25	4
6[a]	2.68 (4) 2.68 (Sty)	$BF_3·OEt_2$	4.0 × 10^{-3}	THF	0 → 25	7[b]

[a] A copolymerization of 4 and styrene. [b] Copolymer contained 38 mol % of 4 according to carbon analysis.

vacuum. AIBN was recrystallized three times from dry methanol and dried in vacuo. Benzene was washed (concentrated H_2SO_4, $NaHCO_3$, distilled water), dried (anhydrous $CaCl_2$), and distilled from sodium/benzophenone before use. NMR and IR spectra were recorded on Varian A60 and Beckman IR-10 spectrometers, respectively. (η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten (4) was prepared as described[24] and purified by sublimation at 50 °C (0.01 mmHg): IR (melt) ν_{CO} 2000, 1915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s, WCH_3), 5.1–5.5 (m, ring and vinyl hydrogens), 6.0–6.5 (m, vinyl). Anal. Calcd for $C_{11}H_{10}O_3W$: C, 35.32; H, 2.69. Found: C, 35.42; H, 2.80.

Copolymerization. Copolymerization experiments were performed in dried deoxygenated benzene at 60 °C in 10-mL Schlenk tubes stirred magnetically. The disappearance of the monomers was followed by GLC. A typical run is described below. Monomer 4, styrene, benzene, and AIBN were weighed into a 10-mL Schlenk tube and deoxygenated under nitrogen by five freeze–pump–thaw cycles. A small aliquot was transferred into a 1-mL vial. The Schenk tube was placed in an oil bath at 60 °C (±0.1 °C). After each sampling for GLC analysis, the system was reinitiated by adding a fresh quantity of AIBN. Reinitiation was followed by three freeze–pump–thaw cycles to deoxygenate and the Schlenk tube was inserted into the oil bath again. The reaction was followed to about 30% conversion.

Analysis of Copolymerization Reactions. In a representative experiment, the analysis of monomers remaining in the reaction mixture as a function of time was carried out by GLC ($^1/_8$ in. × 50 cm, OV-101 (5%) on Chromosorb G-HP (100/200 mesh, injection 150 °C, detector 250 °C, filament 230 °C, reference column Carbowax 20 M, temperature programmed 2 min at 45 °C, 30 °C/min to 160 °C (5 min at 160 °C)). Several injections were made prior to gathering data to demonstrate the system's reproducibility. A Varian Associates Model 3700 gas chromatograph was used and electronic integration was performed with a Hewlett-Packard Model 3380 A recorder–integrator. Samples from a 1-mL reference vial were injected alternately with samples from the polymerization solution which were withdrawn directly from the Schlenk tube. Three injections were averaged to determine the amount of each monomer remaining as a function of time. From these results, the percent conversion and percent incorporation of monomer 4 were calculated. The r_1, r_2, Q, and e values were then computed by using a program prepared in our laboratories.[28]

Anionic and Cationic Initiation. All anionic initiation studies were done with vacuum line techniques. THF was distilled over CaH and further dried by a second distillation from styryllithium immediately before use. Sodium naphthalide was prepared in a dry, preflamed, flask by reacting naphthalene (0.6 g) with sodium metal (0.5 cm^3) in dry THF (100 mL) for 4 h under nitrogen. Preflamed flasks were attached to a vacuum line, dry monomer **4** (0.5 g, 1.34×10^{-3} mol) was added to the reaction flask under nitrogen, and freshly distilled THF (5 mL) was introduced by syringe through an adapter. The resulting solution was twice degassed and then cooled to −78 °C. Next, sodium naphthalide (1×10^{-5} mol, 0.2 mL of a 0.05 mol·L^{-1} solution in THF) was slowly added while the solution was stirred vigorously. The reaction mixture was kept at −78 °C for 1 h and warmed to room temperature, where it was held overnight. Then the solution was poured into dry hexane to precipitate any polymer which had formed. Similar techniques were used in the n-BuLi, $LiAlH_4$, and $BF_3 \cdot OEt_2$ initiated reactions.

Chain Transfer Studies. Polymerizations of styrene with AIBN at 60 °C in the presence of varying amounts of **5–8** were carried out in sealed tubes. The amounts of styrene, AIBN, and benzene were held constant in each tube and varying amounts **5–8** were added to each tube. All tubes were degassed three times by freeze–pump–thaw cycles, sealed under vacuum, and polymerized by a constant-temperature oil bath (60 ± 0.1 °C). The tubes were opened after the specific reaction time and the polymer was precipitated into dry hexane (200 mL). Three reprecipitations were done to purify the polymer which was finally dried in vacuo at 45 °C for 16 h. Intrinsic viscosities were measured in THF at 30 °C, using an Ubbelohde viscometer. The molecular weights were calculated by the Mark–Houwink equation

$$[\eta] = KM^{\alpha}$$

The values of K and α used in these calculations were $K = 1.6 \times 10^{-4}$ and $\alpha = 0.706$.

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