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Polymers and Polymer–Metal Complexes Containing Pendent 2,2′:6′,2″-Terpyridinyl Ligands

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ABSTRACT: Homopolymers and styrene copolymers derived from 4′-vinyl-2,2′:6′,2″-terpyridinyl were prepared in chlorobenzene at 60 °C by using azobis(isobutyronitrile) (AIBN) initiation, and monomer reactivity ratios were determined for the styrene copolymers. These polymeric systems containing pendent terpyridinyl ligands readily formed complexes with Co, Cu, and Zn cations. Although vinylterpyridinyl cobalt and ruthenium complex monomers did not undergo homopolymerization with AIBN initiation, they readily formed styrene copolymers under these polymerization conditions. Removal of the metal ions from these polymer–metal complexes occurred readily on washing the complex with acid.

Polymers containing pendent chelating ligands are of special interest for potential applications as sequestration agents for a variety of metal ions[1] and for the formation of polymer–metal complexes that may behave as redox polymers and homogeneous or heterogenous catalysts.[2,3] Polymer–metal complexes containing 2,2′-bipyridinyl pendent ligands have outstanding properties as redox polymers in chemically modified electrodes[4] and also act as efficient light-harvesting systems in solar energy conversion applications.[5] Poly(vinyl-2,2′-bipyridinyls) were found[6] to be effective sequestration agents for transition metals.

Our interest in terpyridinyl chemistry[7] suggested that incorporation of a vinyl group into various positions on the terpyridinyl nucleus would provide a group of monomers whose homopolymers and styrene copolymers should be of special interest in a number of applications. The established, greater stability[8] of (2,2′:6′,2″-terpyridinyl)metal complexes when compared to the stability of those derived from 2,2′-bipyridinyl indicated that many of the stability problems encountered with polymer–transition metal complexes derived from poly(vinyl-2,2′-bipyridinyl) would be avoided by the use of the terpyridinyl ligand in analogous polymer environments. We have recently found[9] that (vinylterpyridinyl)metal complexes readily undergo electropolymerization yielding modified electrodes containing stable polymer–metal complexes that show interesting electrocatalytic properties. In this publication we show that 4′-vinyl-2,2′:6′,2″-terpyridinyl readily forms homopolymers as well as styrene copolymers using AIBN initiation. The corresponding monomeric metal complexes of cobalt and ruthenium also formed polymer–metal complexes on copolymerization with styrene.

Homopolymers of 4-Vinyl- and 4′-Vinyl-2′:6′,2″-terpyridinyls. Poly(4-vinyl-2,2′:6′,2″-terpyridinyl) (**3**) and poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (**4**) were prepared from 4-vinyl-2,2′:6′,2″-terpyridinyl (**1**) and 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**), respectively, in sealed glass tubes in the presence of a catalytic amount of AIBN in chlorobenzene at 60 °C for 18–24 h. The use of chlorobenzene as solvent resulted in better solubility of the developing polymer and subsequent molecular weight enhancement. The polymers were purified by repeated precipitation into either *n*-hexane or ether from either chlorobenzene or chloroform. The polymers **3** and **4** were isolated as off-white, amorphous materials. Polymer **4** was analyzed thermogravimetrically in a nitrogen atmosphere. The transition onset point was reached at 310 °C, and between 310 and 360 °C the polymer lost most of its weight, and the experiment afforded a char yield of 25%.

Spectroscopic Studies. Homopolymers **3** and **4** were

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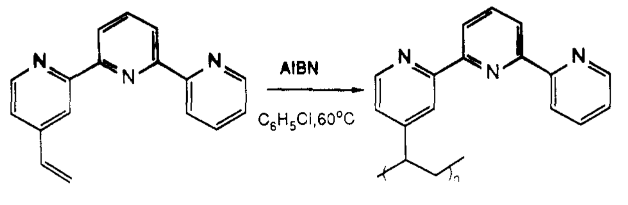

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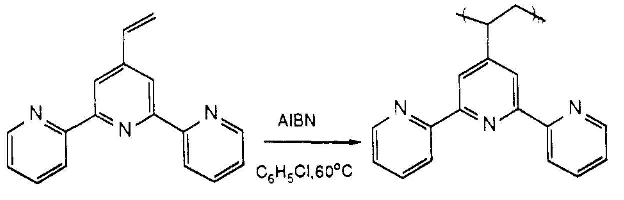


2 4

also characterized by IR, NMR, and elemental analysis data. Molecular weight determinations were made by using gel permeation chromatography and are discussed below. Comparative infrared spectra for 4′-vinyl-2,2′:6′,2″-terpyridinyl (2) and poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4) show a general broadening and the loss of the C=C stretch at 929 cm^{-1} in the IR spectrum of 4. From a comparison of the ^{13}C and ^{13}C APT (attached proton test) spectra (50 MHz) of 4 with the ^{13}C APT spectrum of 2 (Figure 1), it was possible to assign[10] all carbons based on previous ^{13}C NMR studies of 4-vinylpyridine and 2,2′:6′,2″-terpyridinyl. The relative peak broadening in the NMR spectra of polymers is a common phenomenon attributed[11] to the lack of solution mobility of the bulky polymer chains, and in an effort to increase the solution mobility of our polymers, their NMR spectra were measured at elevated temperatures with resultant enhanced resolution (Figures 1 and 2), although this was still poor compared to that in the spectrum of the monomer. Consequently, the absorptions of $C_{2'}$, $C_{4'}$ and C_5, $C_{5''}$, $C_{3'}$, C_5' in the aromatic region are overlapped at δ 154.5 and 120.6, respectively (Figure 1). The methine and methylene carbon absorptions (nearly overlapped at 42.5 ppm in the standard spectrum) were not detectable in the APT spectrum.

The steric bulk of 4′-vinyl-2,2′:6′,2″-terpyridinyl (2) is such that when polymer 4 (derived from 2) was constructed with space-filling models, the syndiotactic form was sterically favored over the isotactic or heterotactic forms, although it was not possible to obtain spectral data that would allow a definitive conclusion to be drawn.

Comparative ^{1}H NMR spectra (200 MHz) for poly(4′-vinyl-2,2′:6′,2″-terpyindyl) (4, dilute solution at room temperature and at 60 °C) and 4′-vinyl-2,2′:6′,2″-terpyridinyl (2, at room temperature) appear in Figure 2. The absence of vinyl hydrogens and the presence of sp^3 hydrogens in the spectrum of 4 indicated polymerization.

Determination of Molecular Weight and Molecular Weight Distribution. The molecular weight distributions of poly(4-vinyl-2,2′:6′,2″-terpyridinyl (3) and poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4) were determined by gel permeation chromatography (GPC), and these results are shown in Table I. All data obtained were based on a calibration curve [log MW versus V_r (retention volume)] constructed by using narrow molecular weight range polystyrene standards, and no correction factors were employed.

The GPC data for hompolymers 3 and especially 4 show these polymers to have very large dispersity indexes ($\bar{M}_w/\bar{M}_n$). A molecular weight distribution curve that tails into the high molecular weight region typically results in a large dispersity index, and a plausible explanation for

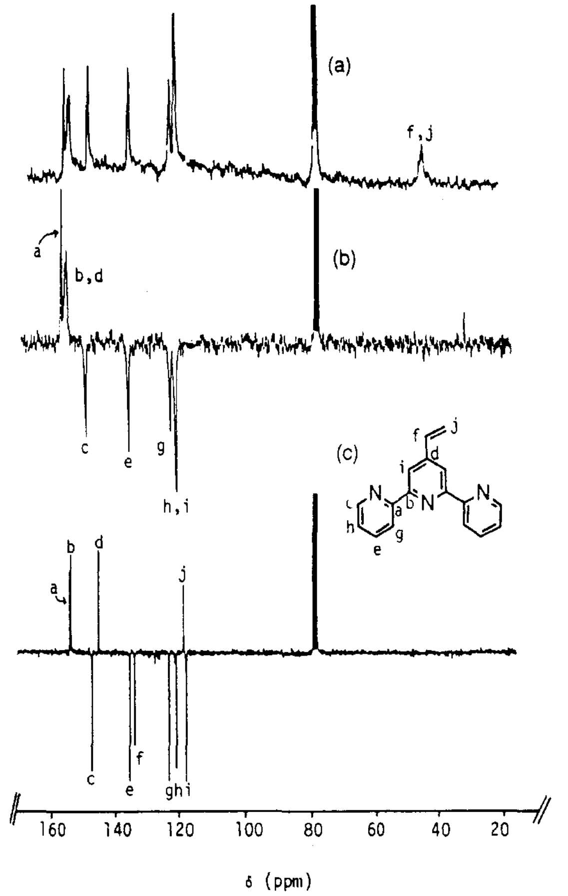


Figure 1. (a) ^{13}C NMR spectrum of poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4, 60 °C); (b) ^{13}C APT spectrum of 4 (60 °C); (c) ^{13}C APT spectrum of 4′-vinyl-2,2′:6′,2″-terpyridinyl (2, room temperature). All spectra were determined in CDCl$_3$ at 50 MHz.

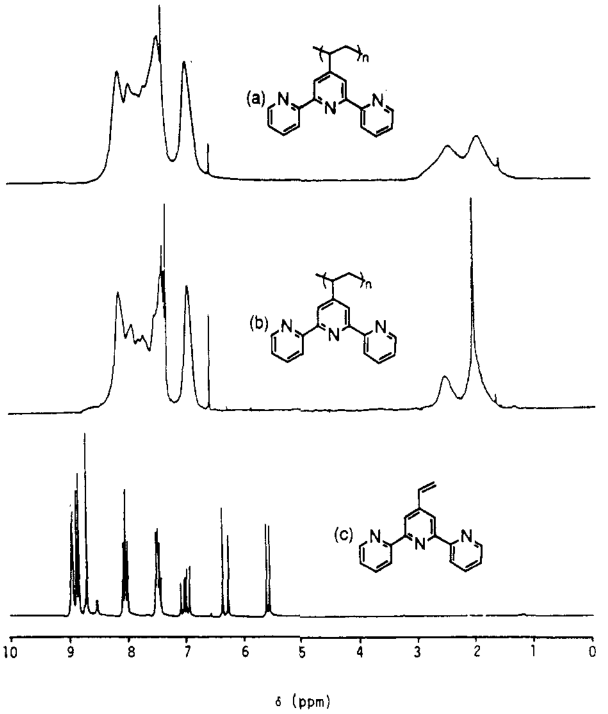


Figure 2. ^{1}H NMR spectra (200 MHz, CDCl$_3$) of poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4): (a) temperature; (b) 60 °C. (c) ^{1}H NMR spectrum of 4′-vinyl-2,2′:6′,2″-terpyridinyl (2), room temperature.

Table I
Homopolymers and Styrene Copolymers Containing Vinylterpyridinyls

polym	$m/(m+n)$ feed	$m(m+n)$ copolym[a]	$\bar{M}_n$ (GPC)[b]	$\bar{M}_w$ (GPC)[b]	$\bar{M}_w/\bar{M}_n$
3	0		10 600	114 800	10.8
4	0		23 000	1 011 000	44.0
5	0.90	0.83	61 700	144 300	2.13
6	0.80	0.71	11 500 (17 500)	35 600 (29 000)	3.09 (1.66)
7	0.50	0.40	62 800	457 700	7.28
8	0.20	0.20	14 500 (2 100)	16 300 (3 500)	1.12 (1.67)
9	0.10	0.064	1 240 (1 260)	6 130 (1 940)	4.97 (1.55)

[a] Determined by elemental analysis (see Experimental Section). [b] GPC values outside of parentheses obtained in our laboratory employing a bank of six Waters ultrastyragel and μ-styragel columns from 10^6- to 100-Å pore sizes, THF solvent, UV detection (254 nm); values in parentheses obtained from General Electric Corporate R&D Center, Schenectady, NY, employing a linear column packed with beads of pore sizes from 10^6 to 500 Å, THF solvent, RI detection. All values were determined versus polystyrene standards.

Table II
Monomer Reactivity Ratios at 60 °C

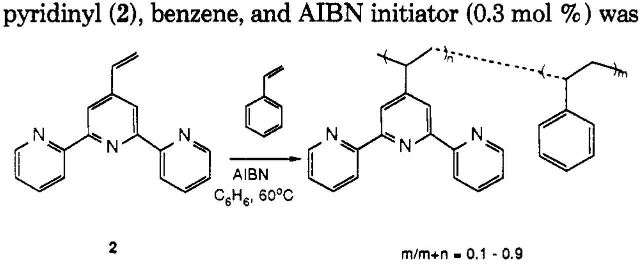
monomer 1	monomer 2	r_1	r_2
styrene	4′-vinyl-2,2′:6′,2″-terpyridinyl	0.47	1.12
	4-vinylpyridine[a]	0.54	0.70
	2-vinylpyridine[a]	0.55	0.90

[a] Data obtained from ref 18.

the above high-dispersity indexes is branching in the polymer backbone. Highly branched polymers commonly have a large high molecular weight tail associated with their molecular weight distribution curves.[13] In consideration of the free-radical polymerization of the monomeric 4′-vinylterpyridinyl to produce poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (**4**), branching could occur after radical extraction of the labile methine hydrogen α to the central pyridine ring in the polymer backbone. The resultant terpyridinyl radical formed could initiate the polymerization of vinylterpyridinyl monomer to produce branched polymer. Extraction of this methine hydrogen is possible either by the initiator or by the growing polymer chain, although the latter (chain transfer to polymer) is the more likely phenomenon since radicals derived from AIBN typically do not attack[14] polymer backbones compared to some other initiator radicals (e.g., benzoyl or lauroyl peroxide). Studies on polystyrene[15] and poly(2-vinylpyridine)[16] have shown that chain transfer to polymer played a significant role in branching in these systems, with chain-transfer constants increasing with increasing temperature.

Copolymers of 4′-Vinyl-2,2′:6′,2″-terpyridinyl and Styrene. 4′-Vinyl-2,2′:6′,2″-terpyridinyl–styrene copolymers were of interest for two main reasons: first, to determine the reactivity ratios of the 4′-vinyl-2,2′:6′,2″-terpyridinyl–styrene system for comparison with the known reactivity ratios of other monomer systems with styrene, particularly the 4-vinylpyridine–styrene system; second, to develop a more economical procedure for building the 2,2′:6′,2″-terpyridinyl unit into a polymer backbone.

The synthetic approach to these copolymers was very similar to that used for the homopolymers above. A mixture of freshly distilled styrene, 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**), benzene, and AIBN initiator (0.3 mol %) was heated to 60 °C in a sealed tube for 20 h. The white, amorphous, and very soluble copolymers **5**–**9** were purified by repeated precipitation into ether or n-hexane from chloroform or chlorobenzene. In addition to IR, NMR, and elemental analysis data, GPC studies were carried out on these copolymers. Unimodal distributions were obtained for all copolymers. These data indicate that copolymers were formed rather than a blend of two homopolymers. Molecular weight and composition data for all these copolymers are in Table I, and all experimental procedures and analytical data are described in the Experimental Section.



2

Determination of Monomer Reactivity Ratios. The reactivity ratios of 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**) and styrene were determined by preparing copolymers **5**–**9** with feed mole percentages of styrene of 90, 80, 50, 20, and 10. These copolymers were analyzed by combustion analysis to determine the percentages of each monomer within the copolymer, and these values are listed in Table I. Utilizing the method[17] of Fineman and Ross, we were able to determine experimentally the reactivity ratios of our monomers from the rearranged version of the copolymer equation:

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}r_1 + r_2$$

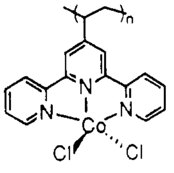
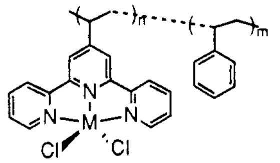
where F_1 = mole fraction of styrene in the copolymer, F_2 = mole fraction of vinylterpyridinyl in the copolymer, f_1 = mole fraction of styrene in the feed, and f_2 = mole fraction of vinylterpyridinyl in the feed.

The left side of the above equation was plotted against the coefficient of r_1 for each of the copolymers to give a straight line with slope r_1 and y-intercept r_2. The reactivity ratios for 4′-vinyl-2,2′:6′,2″-terpyridinyl–styrene calculated from a plot of the above equation are listed in Table II. The values for the 4-vinylpyridine–styrene and 2-vinylpyridine–styrene systems (also determined[18] by the method[17] of Fineman and Ross) are included for comparison.

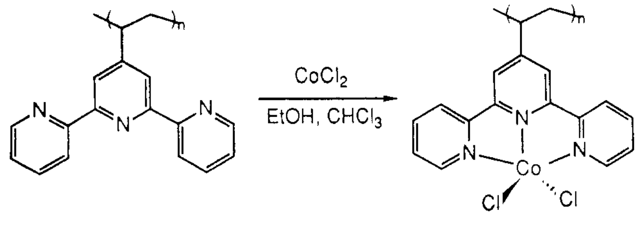
From the mathematical definition of reactivity ratios,[13] where $r_1 < 1$, the propagating monomer 1 would prefer to react with monomer 2. For $r_1 > 1$, the propagating monomer 1 would prefer to react with itself. From Table II for the 4′-vinyl-2,2′:6′,2″-terpyridinyl–styrene system, the r_2 value for the 4′-vinylterpyridinyl was 1.12 and the r_1 value for styrene was 0.47. These data imply that the vinylterpyridinyl radical prefers to react with itself and that the styrene radical also prefers to react with vinylterpyridinyl. For the 4-vinylpyridine–styrene system, however, the 4-vinylpyridine radical ($r_2 = 0.70$) prefers to react with styrene, and the styrene radical ($r_1 = 0.54$) prefers to react with 4-vinylpyridine.

The reasons for the differences in reactivity between the 4-vinylpyridine–styrene system and the 4′-vinyl-2,2′:6′,2″-terpyridinyl–styrene system are not immediately clear. The answer must involve the presence of the 2-pyridinyl substituents in the 2- and 6-positions of the central 4-vinylpyridine ring in the 4′-vinyl-2,2′:6′,2″-terpyridinyl monomer. These substituents would exert a stabilizing influence on the developing radical after this monomer has added to the propagating chain.

Table III
Polymer–Metal Complexes via Reaction of Polyligands with Transition-Metal Cations

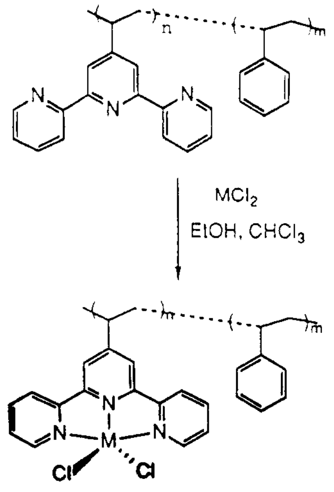
complex	M	*m*/(*m* + *n*)	mol formula	anal. data calcd (found) C	H	N
						
10			$(C_{17}H_{13}N_3CoCl_2{\cdot}H_2O)_n$	50.14 (49.73)	3.72 (3.79)	10.31 (10.22)
						
11	Co	0.40	$(C_{13.35}H_{10.97}N_{1.79}Co_{0.595}Cl_{1.19}{\cdot}0.595H_2O)_n$	56.37 (56.80)	4.32 (4.72)	8.79 (9.08)
12	Zn	0.71	$(C_{10.90}H_{9.45}N_{0.867}Zn_{0.289}Cl_{0.578}{\cdot}0.578H_2O)_n$	64.04 (63.64)	4.80 (5.08)	6.11 (6.22)

Preparation of Polymer–Metal Complexes. Synthesis via Reaction of Poly(vinylterpyridinyls) with Transition-Metal Cations. The polyligands prepared above readily reacted with transition-metal ions in solution to produce colored polymer–metal complexes. Reaction of poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4) with $CoCl_2$, $CuCl_2$, and $ZnCl_2$ resulted in an immediate precipitation of polymer–metal complexes. Being completely insoluble in all common solvents, the deep-green cobalt complex was purified by numerous washings with copious quantities of ethanol and chloroform and was shown to be the 1:1 complex represented by 10.



4 10

Similarly, the styrene copolymers 6 and 7 reacted readily with $ZnCl_2$ and $CoCl_2$ to produce 1:1 polymer–metal complexes 11 and 12 as determined by elemental analysis (Table III). These complexes were also characterized by IR data (Experimental Section).

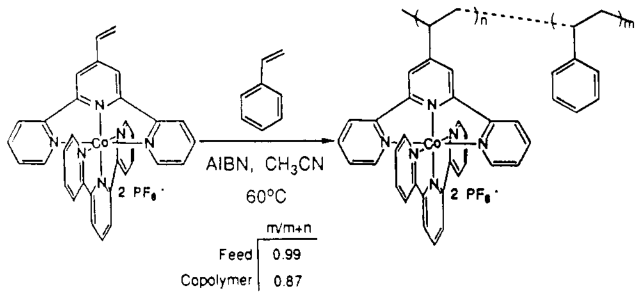


11; m/m+n = 0.40, M = Co
12 ; m/m+n = 0.71, M = Zn

It is particularly interesting that the polyligand reactions with cobaltous chloride resulted in 1:1 polymer–metal complexes. This is in direct contrast to the coordination behavior of monomeric 2,2′:6′,2″-terpyridinyl, where both thermodynamic and kinetic factors favor[8] exclusive formation of octahedral bis(ligand)cobalt complexes. With uilitization of poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) as the ligand, 1:1 cobalt–terpyridinyl complexes were always obtained, even in the reaction employing the styrene copolymer 7. These results suggest that in these pendent-ligand polymer systems the spatial arrangement of the pendent ligands is such that bis(ligand)metal complex formation is impossible. The metal ions could be removed from the polymer by repeated washing with hot, concentrated hydrochloric acid solution followed by filtration and recovery of the uncomplexed polymer. It should be noted that similar 1:1 polymer–metal complexes were formed[19] from poly[1-(6,6′-dimethyl-2,2′-bipyridin-5-yl)ethylene] with $CoCl_2$, $CuCl_2$ and $ZnCl_2$. Similar solubilities were also observed for this group of polymer metal complexes.

Synthesis via Polymerization of (Vinylterpyridinyl)metal Complex Monomers. Synthesis of polymer–metal complexes via modification of polyligands with metal cations has been reported[20] to result in unreacted (and thus underutilized) ligands in the polystyryl(2,2′-bipyridinyl) series. The more direct, unambiguous method of directly polymerizing or copolymerizing (2,2′-bipyridinyl)metal complex monomers has only been briefly exploited.[6,21] The polymerization of (vinylterpyridinyl)metal complex monomers was of special interest in our study because this method offered a direct route to polymers incorporating simple or mixed-ligand complexes in the backbone. Attempts to homopolymerize these complexes in solution at 60 °C with AIBN initiation failed, although these complex monomers readily formed homopolymers on electrode reduction.[9] In contrast, styrene copolymers were synthesized successfully. The choices of reaction solvent and complex monomer counterion were found to be most important in determining whether the copolymerization occurred. The polymerization was unsuccessful with perchlorate as the counterion, possibly because the perchlorate ion is a potent oxidizing agent. The counterion was readily changed from perchlorate to hexafluorophosphate by using Dowex IX8-50 ion-exchange resin (chloride form) and treating the recovered eluant with aqueous ammonium hexafluorophosphate. From solvents such as dimethylacetamide, dimethylformamide (DMF), and CH_3CN, only in CH_3CN did the copolymerization occur. This effect may simply be due to the superior solubility of the complex monomers in CH_3CN.

Two systems were copolymerized with styrene to produce copolymer–metal complexes. In the first instance, (4′-vinyl-2,2′:6′,2″-terpyridinyl)(2,2′:6′,2″-terpyridinyl)cobalt(II) hexafluorophosphate[9] (13 1 mol %) and freshly distilled styrene (99 mol %) were copolymerized in acetonitrile in a sealed tube with a catalytic amount of azobis(isobutyronitrile) (AIBN) at 60 °C for 20 h, and the copolymer was washed thoroughly with chloroform to remove any polystyrene impurity. This process resulted in the light-brown amorphous copolymer–cobalt complex 14 containing 87 mol % styrene by elemental analysis. Complex 14 was purified by repeated precipitation from DMF into ether.

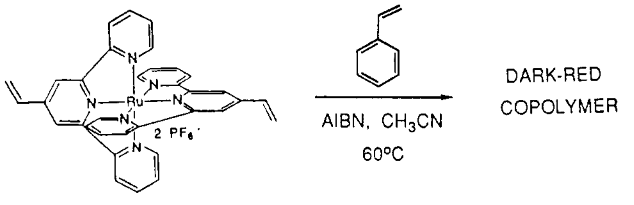


13

14

The copolymerization of mixed-ligand monomer 13 with styrene produced copolymer 14 containing pendent cobalt complexes all along the polymer backbone. Complex 14 was analyzed by IR, UV–vis spectroscopy, and elemental analysis, and full details are reported in the Experimental Section.

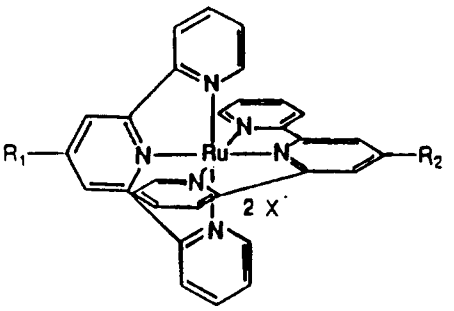
The second system copolymerized with styrene was bis(4′-vinyl-2,2′:6′,2″-terpyridinyl)ruthenium(II) hexafluorophosphate[9] (15). Because monomer 15 contained two vinyl groups, the introduction of 15 into a copolymer would result in cross-linking if both vinyl groups polymerized. With reaction conditions similar to those described above, 15 and freshly distilled styrene (99 mol %) were copolymerized in a sealed tube to produce, after washing with copious quantities of chloroform and several precipitations from DMF into ether, the dark red amorphous copolymer 16 containing 95% styrene (by elemental analysis).



15

Relating copolymer 16 to the insoluble styrene/5% divinylbenzene copolymer system, one would expect the introduction of 5% divinyl complex monomer to result in a completely insoluble, highly cross-linked copolymer if both vinyl groups of the metal complex polymerized. Since copolymer 16 was soluble in DMSO, DMF, and CH_3CN (and even filtered through Whatman number 1 filter paper), we immediately suspected that the system (a) was not completely crosslinked, i.e., that both complex vinyl groups had not polymerized, or (b) the copolymer had a very low molecular weight. Probing the polymer structure was best effected by utilizing ultraviolet–visible spectroscopy. Other spectroscopic methods employed (e.g., ^1H NMR, IR) gave indefinite results. Comparable UV–vis data for several monomeric complexes and copolymer 16 appear in Table IV.

Table IV
Comparative UV-Vis Data for Several Complex Monomers and Copolymer 16



R_1	R_2	UV-vis (CH_3CN) λ_{max}, nm
H	H	475, 308, 271, 230
vinyl	vinyl	489, 313, 274, 241
vinyl	H	482, 309, 273
$-CH_3$	$-CH_3$	476, 308, 271
$-CHCH_2$		482, 310, 275, 235

The UV–vis absorption maxima of the monomeric complexes were sensitive to the substituent(s) on the ligands. From Table IV, the bathochromic shift resulting from the introduction of a vinyl substituents(s) on the ligand is clearly seen. From comparison of the data for copolymer 16 to that for the monomers in Table IV, the visible absorption of copolymer 16 at 482 nm points to the presence of a vinyl group on complexes within the copolymer. Although more definitive structural data are lacking, these present data do provide insight into the microstructure of this copolymer–metal complex. No molecular weight data were obtained for this system, solvent incompatibility with GPC being the major obstacle.

Experimental Section

General spectral characterizations were carried out on the following instruments: infrared spectra, Perkin-Elmer Model 298 or 337 grating infrared spectrophotometer; ultraviolet–visible spectra, Varian Cary Model 219 ultraviolet–visible spectrophotometer; ^{13}C and ^1H NMR spectra, Varian XL-200. Differential scanning calorimetry and thermogravimetric analysis determinations were carried out on computer-assisted Perkin-Elmer Model 7500 Series 7 TGA and DSC analyzers with platinum or aluminum sample pans. Gel permeation chromatographic determinations were carried out by using a bank of six Waters μ-styragel and ultrastyragel columns in series from 100- to 10^6-Å pore sizes. Injections were made on a Waters Model 6000A analytical HPLC system utilizing UV detection (254 nm). Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA, and the polymers were dried at 100 °C under high vacuum (10^{-6} mmHg) for 48 h before analysis.

Anhydrous solvents and reagents were prepared and stored as follows: *N*,*N*-dimethylformamide (DMF), dried over CaH_2, refluxed and distilled under reduced pressure, and stored over 4-Å molecular sieves; toluene, benzene, xylene, *n*-hexane, and diethyl ether stored over metallic sodium and decanted; styrene, washed with 10% NaOH and then H_2O (to remove inhibitor), dried over anhydrous sodium sulfate for 24 h, and fractionally distilled under nitrogen at reduced pressure in the presence of cuprous chloride; acetonitrile, dried over calcium sulfate for 18 h, then fractionally distilled, and stored over 4-Å molecular sieves; chlorobenzene, dried over anhydrous sodium sulfate and fractionally distilled under reduced pressure.

Monomeric ligands and transition-metal complexes were prepared as previously described.[9]

Poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (4). A 50-mL ampule was charged with 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**, 500 mg, 1.93 mmol), freshly distilled chlorobenzene (9 mL), and AIBN (1.0 mg, 6.1×10^{-3} mmol, 0.3%). After three freeze–thaw degassing cycles, the ampule was sealed under vacuum and heated to 60 °C for 19 h. After the ampule was cooled, it was opened, and the pale-yellow solution was added slowly to a stirred ether solution (150 mL). A white solid immediately precipitated and was collected on a frit. Reprecipitation (3×) from chlorobenzene into ether afforded a pale-yellow amorphous solid: 460 mg (92%), T_g = 202 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.26–5.22 (m, 10, aromatic), 1.69 (s, 1, C*H*CH$_2$), 1.25 (s, 2, CHCH_2); ^{13}C NMR ($CDCl_3$) δ 155.87, 154.59, 154.16, 148.33, 135.67, 122.62, 120.60; IR (KBr) $\nu_{C=N}$ 1590 and 1570 cm^{-1} (s); $\bar{M}_n$ (GPC) = 23 000, $\bar{M}_w$ (GPC) = 1 011 000, $\bar{M}_w/\bar{M}_n$ = 43.97.

Anal. Calcd for $(C_{17}H_{13}N_3 \cdot 0.33H_2O)_n$: C, 76.98; H, 5.19; N, 15.84. Found: C, 77.29; H, 5.19; N, 15.83.

Poly(4-vinyl-2,2′:6′,2″-terpyridinyl) (3). A 50-mL ampule was charged with 4-vinyl-2,2′:6′,2″-terpyridinyl (**2**, 230 mg, 0.93 mmol), freshly distilled chlorobenzene (5 mL), and AIBN (0.40 mg, 2.44×10^{-3} mmol, 0.3%). After three freeze–thaw degassing cycles, the tube was sealed under vacuum and heated to 60 °C for 20 h. After the ampule was cooled, it was opened, and its contents were added to stirring ether (150 mL). A white solid was forced out of solution and was collected on a frit. Reprecipitation (3×) from chlorobenzene into ether afforded a pale-yellow amorphous solid: 150 mg (65%); IR (KBr) $\nu_{C=N}$ 1560 and 1580 cm^{-1} (s); $\bar{M}_n$ (GPC) = 10 600, $\bar{M}_w$ (GPC) = 114 800, $\bar{M}_w/\bar{M}_n$ = 10.80.

General Procedure for the Preparation of Vinylterpyridinyl–Styrene Copolymers. Synthesis of Poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (7). A 50-mL ampule was charged with 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**, 80 mg, 0.31 mmol), freshly distilled benzene (5 mL), freshly distilled styrene (0.036 mL, 0.31 mmol), and AIBN (0.21 mg, 0.001 24 mmol, 0.2%). After three freeze–thaw degassing cycles, the tube was sealed under vacuum and heated to 60 °C for 19 h. After the ampule was cooled, it was opened, and its contents were added to stirring ether. A white fibrous solid precipitated and was collected on a frit. Reprecipitation (3×) from chlorobenzene into ether afforded a white amorphous solid: 100 mg (88% conversion of monomers); IR (KBr) ν_{OH} 3600–3510, ν_{CH} 2910 (w), $\nu_{C=N}$ 1590 and 1610 cm^{-1} (s); $\bar{M}_n$ (GPC) = 62 800, $\bar{M}_w$ (GPC) = 457 700, $\bar{M}_w/\bar{M}_n$ = 7.28.

Anal. Calcd for $(C_{13.35}H_{10.97}N_{1.79} \cdot 0.298H_2O)_n$ where [sty]/([sty] + [v-terpy]) = 0.404: C, 79.48; H, 5.79; N, 12.40. Found: C, 79.84; H, 5.66; N, 12.54.

Poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (5). Following the above procedure with **2** (50 mg, 0.19 mmol), freshly distilled styrene (0.20 mL, 1.74 mmol), AIBN (0.003 86 mmol, 0.63 mg, 0.2%), and benzene (5 mL) resulted in 100 mg of **5** (43% conversion of monomers); $\bar{M}_n$ (GPC) = 67 800, $\bar{M}_w$ (GPC) = 144 300, $\bar{M}_w/\bar{M}_n$ = 2.13.

Anal. Calcd for $(C_{9.58}H_{8.80}N_{0.525} \cdot 0.175H_2O)_n$ where [sty]/([sty] + [v-terpy]) = 0.825: C, 85.30; H, 6.91; N, 5.45. Found: C, 85.58; H, 6.77; N, 5.51.

Poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (6). Following the above procedure with **2** (200 mg, 0.77 mmol), freshly distilled styrene (0.35 mL, 3.08 mmol), AIBN (1.90 mg, 0.0116 mmol, 0.3%), and benzene (5 mL) resulted in 180 mg of **6** (36% conversion of monomers); $\bar{M}_n$ (GPC) = 11 500; $\bar{M}_w$ (GPC) = 35 600; $\bar{M}_w/\bar{M}_n$ = 3.09.

Anal. Calcd for $(C_{10.60}H_{9.445}N_{0.867})_n$ where [sty]/([sty] + [v-terpy]) = 0.711: C, 85.45; H, 6.40; N, 8.15. Found: C, 85.16; H, 6.45; N, 8.13.

Poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (8). Similarly, with **2** (252 mg, 0.972 mmol), freshly distilled styrene (0.028 mL, 0.25 mmol), AIBN (0.59 mg, 0.0037 mmol, 0.3%), and benzene (5 mL) there was obtained 150 mg of **8** (54% conversion of monomers); $\bar{M}_n$ (GPC) = 14 500; $\bar{M}_w$ (GPC) = 16 300; $\bar{M}_w/\bar{M}_n$ = 1.12.

Anal. Calcd for $(C_{15.18}H_{11.99}N_{2.394})_n$ where [sty]/([sty] + [v-terpy]) = 0.202: C, 79.98; H, 5.31; N, 14.71. Found: C, 79.76; H, 5.33; N, 14.80.

Poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (9). Similarly, **2** (257 mg, 0.99 mmol), freshly distilled styrene (0.013 mL, 0.11 mmol), AIBN (0.54 mg, 0.0033 mmol, 0.3%), and benzene ((5 mL) gave 190 mg of **9** (71% conversion of monomers); $\bar{M}_n$ = 1240; $\bar{M}_w$ = 6130; $\bar{M}_w/\bar{M}_n$ = 4.97.

Anal. Calcd for $(C_{16.43}H_{12.68}N_{2.808})_n$ where [sty]/([sty] + [v-terpy]) = 0.0643: C, 77.91; H, 5.06; N, 15.53. Found: C, 78.72; H, 5.26; N, 15.60.

Poly(4′-vinyl-2,2′:6′,2″-terpyridinyl)cobalt(II) Dichloride Monohydrate (10). A 10-mL flask was fitted with a nitrogen inlet and charged with poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (**4**, 40 mg, 0.15 mmol) and chloroform (5 mL). After the solution was homogeneous, cobaltous chloride (19 mg, 0.15 mmol) in absolute ethanol (2 mL) was added to the reaction solution, which immediately became dark green and heterogeneous. After stirring for 24 h under N_2, all solvent was evaporated to afford a dark-green, insoluble, amorphous polymer–metal complex, which was collected and washed with copious quantities of absolute ethanol and chloroform and then air dried: 59 mg (99%); IR (KBr) ν_{OH} 3600–3200 (m), $\nu_{C=N}$ 1600 cm^{-1} (s) (Table III).

Poly[((4′-vinyl-2,2′:6′,2″-terpyridinyl)cobalt(II) dichloride monohydrate)-*co*-styrene] (11). A 25-mL flask was fitted with a nitrogen inlet and charged with poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (**7**, [sty]/([sty] + (v-terpy]) = 0.40, 40 mg, 0.11 mmol, 0.055 mmol of terpyridinyl units) and chloroform (15 mL). After homogeneity was achieved, cobaltous chloride (8.0 mg, 0.062 mmol) in absolute ethanol (3 mL) was added to the solution, which became immediately dark green and heterogeneous. After stirring under nitrogen at room temperature for 24 h, all solvent was removed to give an insoluble, dark-green, amorphous polymer–metal complex, which was collected and washed with copious quantities of absolute ethanol and chloroform: 45 mg (96%); IR (KBr) ν_{OH} 3600–3200 (m), ν_{CH} 2900 (w), $\nu_{C=N}$ 1600 cm^{-1} (s) (Table III).

Poly[((4′-vinyl-2,2′:6′,2″-terpyridinyl)zinc(II) dichloride dihydrate)-*co*-styrene] (12). A 25-mL flask was fitted with a nitrogen inlet and charged with poly[(4′-vinyl-2,2′:6′,2″-terpyridinyl)-*co*-styrene] (**6**, [sty]/([sty] + [v-terpy]) = 0.711, 50 mg, 0.26 mmol, 0.080 mmol of terpyridinyl units) and chloroform (5 mL). After the solution was homogeneous, zinc(II) dichloride (14 mg, 0.10 mmol) in absolute ethanol (1 mL) was added, and the solution immediately turned bright yellow and became heterogenous. After 24 h of stirring under nitrogen at room temperature, all solvent was removed, producing a yellow, amorphous polymer–metal complex. Reprecipitation from DMF into ether produced a bright-yellow complex: 55 mg (90%); IR (KBr) ν_{OH} 3700–3200 (s), ν_{CH} 3010 and 2910 (m), $\nu_{C=N}$ 1595 cm^{-1} (s).

Anal. Calcd for $(C_{10.60}H_{9.45}N_{0.867}Zn_{0.289}Cl_{0.578} \cdot 0.578H_2O)_n$ where [sty]/([sty] + [Zn^{II} complex]) = 0.711: C, 64.04; H, 4.80; N, 6.11. Found: C, 63.64; H, 5.08; N. 6.22.

Poly[((4′-vinyl-2,2′:6′,2″-terpyridinyl)(2,2′:6′,2″-terpyridinyl)cobalt(II) hexafluorophosphate monohydrate)-*co*-styrene] (14). A 50-mL ampule was charged with (4′-vinyl-2,2′:6′,2″-terpyridinyl)(2,2′:6′,2″-terpyridinyl)cobalt(II) hexafluorophosphate (**13**, 60 mg, 0.0713 mmol), freshly distilled styrene (0.81 mL, 7.06 mmol), AIBN (9.37 mg, 0.057 mmol, 0.8%), and freshly distilled acetonitrile (8 mL). After three freeze–thaw degassing cycles, the ampule was sealed under vacuum and heated to 60 °C for 20 h. During this time, the dark-brown homogeneous solution became lighter colored and heterogeneous. After cooling, the ampule was opened, and its viscous contents were added to stirring ether, causing a light-brown solid to separate. This product was washed with chloroform and, after several reprecipitations from DMF into ether, a light-brown, amorphous polymer–metal complex was isolated: 190 mg (24% conversion of monomers); IR (KBr) ν_{OH} 3600–3100 (m), ν_{CH} 3090, 3070, 3010, and 2910 (m), $\nu_{C=N}$ 1600 (m), $\nu_{PF_6^-}$ 840 cm^{-1} (s); λ_{max} (CH_3CN) 320, 281, 276 nm.

Anal. Calcd for $(C_{11.08}H_{10.05}N_{0.768}P_{0.256}F_{1.54}Co_{0.128} \cdot 0.256H_2O)_n$ where [sty]/([sty] + [Co^{2+} complex]) = 0.872: C, 65.46; H, 5.00; N, 5.30. Found: C, 65.72; H, 5.27; N, 5.30.

Poly[(bis(4′-vinyl-2,2′:6′,2″-terpyridinyl)ruthenium(II) hexafluorophosphate monohydrate)-*co*-styrene] (16). A 50-mL ampule was charged with bis(4′-vinyl-2,2′:6′,2″-terpyridinyl)ruthenium(II) hexafluorophosphate **15**, 50 mg, 0.055 mmol), freshly distilled styrene (1.25 mL, 10.9 mmol), AIBN (14.5 mg, 0.088 mmol, 0.8%), and freshly distilled acetonitrile (6 mL). After three freeze–thaw degassing cycles, the ampule was sealed under vacuum and heated to 60 °C for 20 h. During this time, the deep-red homogeneous solution turned a lighter color and became heterogeneous. After cooling, the tube's viscous contents were added to stirring ether, and a dark-red solid separated. This precipitate was collected on a frit, washed with chloroform, and reprecipitated several times from DMF into ether to afford a dark-red amorphous polymer–metal complex: 200 mg (17% conversion of monomers); IR (KBr) ν_{OH} 3650–3150 (m), ν_{CH} 3090, 3070, 3010, and 2910 (m), $\nu_{C=N}$ 1600 (m), $\nu_{PF_6^-}$ 840 cm^{-1} (s); λ_{max} (CH_3CN) 482, 310, 275, 235 nm.

Anal. Calcd for $(C_{9.24}H_{8.86}N_{0.285}P_{0.0952}F_{0.571}Ru_{0.0476}\cdot 0.0476H_2O)_n$ where [sty]/([sty] + [Ru^{2+} complex]) = 0.952: C, 77.38; H, 6.37; N, 2.79. Found: C, 77.13; H, 6.35; N, 2.79.

Registry No. 2, 108295-34-7; **3**, 114532-87-5; **4**, 114532-88-6; (**4**)(styrene) (copolymer), 114532-89-7; (**13**)(styrene) (copolymer), 114532-90-0; (**15**)(styrene) (copolymer), 114532-92-2; styrene, 100-42-5.

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Cyclopolymerization of Dipropargylsilanes by Transition-Metal Catalysts

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ABSTRACT: Polymerization of dipropargylsilanes [$RR'Si(CH_2C{\equiv}CH)_2$; R, R' = CH_3 or Ph] was examined for various transition-metal catalyst systems. A molybdenum complex was found to be a particularly effective catalyst for the cyclopolymerization of dipropargylsilanes. Polymerization of methylphenyldipropargylsilane and diphenyldipropargylsilane by various catalysts leads to soluble, highly colored polymers of average molecular weight 7000–15000. Polymerization of dimethyldipropargylsilane under the same conditions, however, gives only a partially soluble polymer. IR, ^1H NMR, and UV-visible spectroscopies showed that poly(methylphenyldipropargylsilane) and poly(diphenyldipropargylsilane) possess polyene structures having cyclic recurring units in the polymer backbone. Poly(dipropargylsilane)s have been investigated in terms of physical properties, the nature of the doping process, electrical conductivity, and thermal and oxidative stability. The size of substituents was important for the cyclopolymerization tendency and for the resulting polymer properties.

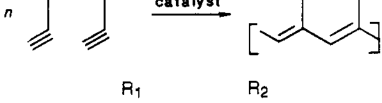
Introduction

There have been many studies of polyacetylene[1] because of its unique properties. Polyacetylene is, however, unstable in air and insoluble in the usual organic solvents. Thus, though the electrical conductivity is somewhat low, a study of the synthesis and properties of substituted polyacetylene has been intensively investigated.[2]

Since various substituted acetylenes have been polymerized by transition-metal catalysts to olefinic polymers, the cyclopolymerizations of nonconjugated diynes were investigated in an attempt to prepare a polymer that would contain alternating double and single bonds along the polymer backbone and a cyclic recurring unit.[3] Recently, Gibson et al. reported that the polymerization of 1,6-heptadiyne by a special method using a Ziegler–Natta catalyst [$Ti(OBu)_4/Et_3Al$] leads to insoluble polymer films.[4]

In another work,[5] we have found that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of dipropargyl sulfide and dipropargyl ether.

The present paper deals with the cyclopolymerization by Mo- and W-based catalysts of dipropargylsilanes, which often has an interesting character (see eq 1).



(1)

R1	R2
CH_3	CH_3
CH_3	C_6H_5
C_6H_5	C_6H_5

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