The Vinyl Reactivity of (η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium. A Novel Vinyl Organometallic Monomer

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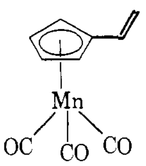
ABSTRACT: The novel vinyl organometallic monomer (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (hereafter called vinylcynichrodene),[40] recently prepared, was homopolymerized and copolymerized in the presence of azo initiators, both neat and in benzene solutions. Reactivity ratios were obtained in radical-initiated copolymerizations with styrene and *N*-vinyl-2-pyrrolidone.[41] When M_2 was styrene, $r_1 = 0.30$ and $r_2 = 0.82$. The value of the Alfrey–Price parameter *e* for vinylcynichrodene was evaluated as −1.98. The resonance interaction parameter *Q* was 3.1 for vinylcynichrodene. Copolymerizations with *N*-vinyl-2-pyrrolidone (M_2) gave $r_1 = 5.3$, $r_2 = 0.079$, and $e_1 = -2.07$. Thus, it is clear that vinylcynichrodene is an exceptionally electron-rich vinyl monomer resembling vinylferrocene and vinylcymantrene. Vinylcynichrodene readily copolymerized with vinylcymantrene and homopolymerized in high yields in ethyl acetate solution. The molecular weight of poly(vinylcynichrodene) increased as the monomer to initiator ratio increased suggesting that the rate was not first order in initiator as had been found previously in vinylferrocene polymerizations.

The synthesis of organometallic polymers[2–5] and studies of their novel properties[2–7] have accelerated in scope in recent years. The radical-initiated addition homopolymerization and copolymerization of a variety of transition-metal-containing monomers has been under intense study in our laboratory. For example, studies of organometallic monomers including η^6-styrenetricarbonylchromium,[8] vinylcymantrene,[1,9] vinylferrocene,[10] η^6-(benzyl acrylate)tricarbonylchromium,[11] ferrocenylmethyl acrylate,[12,13] η^6-(2-phenylethyl acrylate)tricarbonylchromium,[14] as well as 2-ferrocenylethyl acrylate[15] and methacrylate[15] have now appeared. Recently, a comprehensive review of vinyl addition polymerization of organometallic monomers appeared.[16]

Addition polymerization studies of organometallic carbonyl monomers are rare, indeed, compared with metallocenes.[3] Organochromium monomer syntheses and polymerizations are restricted to the three examples: η^6-styrenetricarbonylchromium,[8] η^6-(benzyl acrylate)tricarbonylchromium,[11] and η^6-(2-phenylethyl acrylate)tricarbonylchromium.[14] Vinylcymantrene,[1] **1**, is isoelectric with vinylcynichrodene, **2**. Since vinylcymantrene's copolymerization reactivity with a series of organic monomers has now been defined,[1,17] it was of interest to see how changing the metal fragment from $Mn(CO)_3$ to $Cr(CO)_2NO$ would affect the monomer reactivity.



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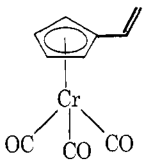

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We now report the addition, homopolymerization, and copolymerization of the novel monomer, vinylcynichrodene, **2**. To our knowledge, this represents the first example of the polymerization of an organometallic monomer containing a nitrosyl (NO) substituent. Furthermore, we demonstrate that changing the metallic fragment from $Mn(CO)_3$ to $Cr(CO)_2NO$ did not exert drastic effects on the reactivity of the vinyl group. In both 1 and 2 the vinyl group was exceedingly electron rich.

Results and Discussion

Pittman et al.[2,3,8–17] have recently described comprehensive studies of the addition polymerization reactivity of vinylorganometallic monomers. It has been found that transition metal organometallic functions, when attached to a vinyl group, often exert enormous effects on addition polymerization reactivity.[16,17] For example, vinylcymantrene 1 and vinylferrocene, when classified according to the Alfrey–Price *Q–e* scheme,[18,19] exhibit *e* values of −1.99 and −2.1, respectively, in copolymerizations with styrene. This means the vinyl group in both these organometallic monomers is more electron rich than that of 1,1-bis(*p*-anisyl)ethylene (*e* = −1.96).[19] In order to extend the series of organometallic monomers, vinylcynichrodene, **2**, was synthesized and polymerized.

Cynichrodene, **3** (Scheme I), was first prepared by Fischer et al. in 1955.[20] Since that time very little chemistry of this complex has appeared. It was acylated in good yield by Fischer and Plesske[21] but the chemistry remained largely unexplored. Recently, we prepared vinylcynichrodene, **2**, according to Scheme I.[22] Cynichrodene was acetylated in 50–65% yield, followed by sodium borohydride reduction of the carbonyl group (88%) and *p*-toluenesulfonic acid-catalyzed dehydration (70–86%) of the resulting alcohol in the presence of hydroquinone as a radical inhibitor. Vinylcynichrodene is a red liquid, bp 79–80 °C (0.3 mmHg), which was conveniently purified by filtration through alumina and repeated vacuum distillation.

Purification is particularly important because alcohol, **5**, readily forms its ethyl ether if traces of ethanol are present in the dehydration step. Furthermore, small amounts of the dimeric ether of 5 are also formed during dehydration. The IR and NMR spectra of **2**, used in this work, were in accord with structure and a satisfactory analysis was obtained (see Experimental Section). In addition, GLC studies of 2 were made to monitor its purity.

Copolymerization. Vinylcynichrodene was homopolymerized and copolymerized with styrene, *N*-vinyl-2-pyrrolidone, and vinylcymantrene (Scheme II). Azo initiators were used in each case. A series of copolymerizations with styrene were carried out to determine the reactivity ratios of **2**. Styrene was chosen because it had previously been used in reactivity ratio studies with vinylferrocene and vinylcymantrene, **1**.[2a,17] Furthermore, styrene is a moderately electron-rich monomer (*e* = −0.80). We anticipated that if **2** were a very electron-rich monomer, resembling **1**, the use of electron attracting comonomers (i.e., acrylonitrile or methyl acrylate) might result in

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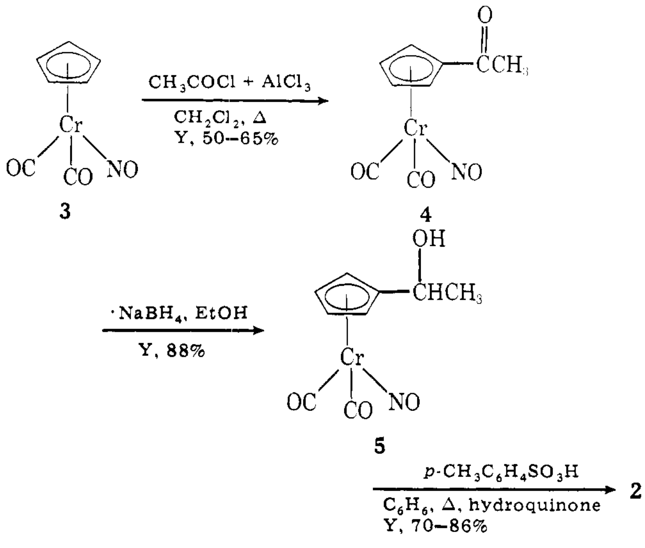
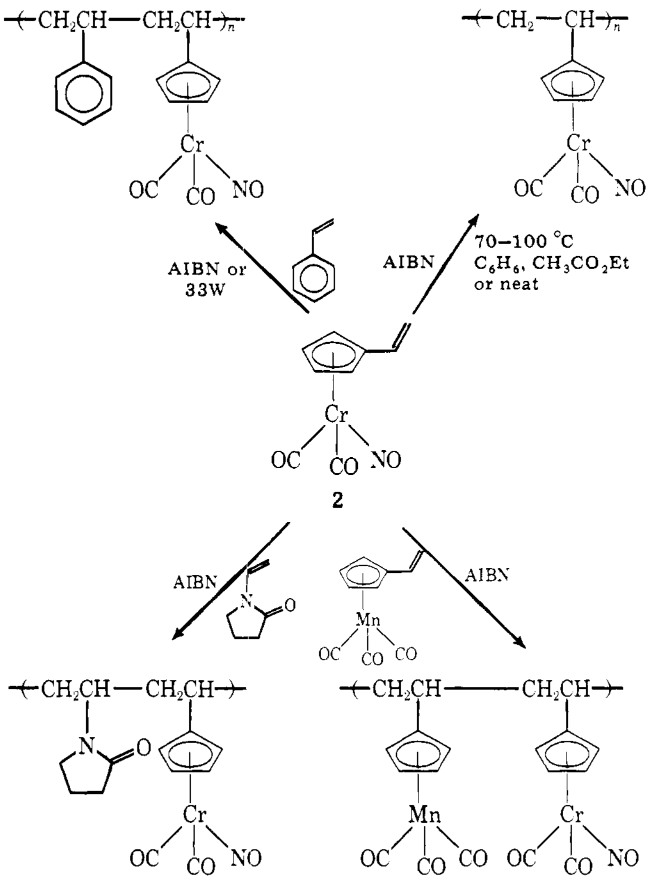
Scheme I



Scheme II



failure of the Q–e scheme, similar to that observed for both vinylferrocene and 1 when copolymerized with electron attracting monomers.[17]

Table I
Composition–Conversion Data for Copolymerizations of Vinylcynichrodene, 2, with Styrene (M_2) [a]

Run	Vinylcynichrodene in feed, mol %	Conversion, %	Vinylcynichrodene in copolymer, mol %
1	48.4	30.1	41.2
2a	69.9	6.77	58.6
2b	69.9	8.53	54.5
2c	69.9	12.15	56.8
2d	69.9	15.29	57.2
2e	69.9	17.58	58.6
2f	69.9	19.33	57.7
3a	28.7	6.75	25.6
3b	28.7	11.51	28.7
3c	28.7	26.74	25.5
3d	28.7	26.79	27.9
3e	28.7	28.71	26.5
4a	83.1	7.76	66.3
4b	83.1	8.43	69.1
4c	83.1	10.24	71.0
4d	83.1	9.77	69.2
4e	83.1	9.11	67.4
4f	83.1	10.37	70.0
4g	83.1	10.49	69.2
4h	83.1	13.78	70.0
4i	83.1	15.36	70.6
4j	83.1	12.25	64.4
4k	83.1	15.17	69.7

[a] From these data the calculated reactivity ratios for this monomer pair are $r_1 = 0.30$ and $r_2 = 0.82$.

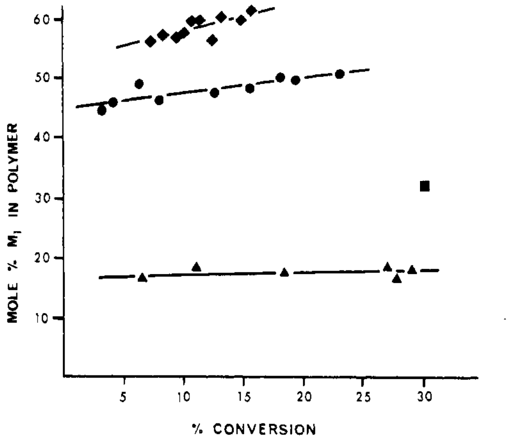


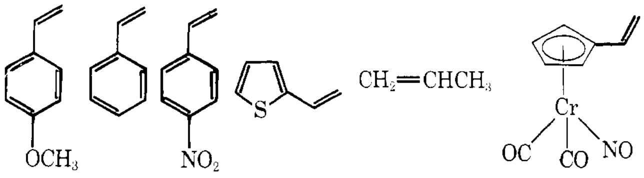
Figure 1. Composition–conversion plots for example vinylcynichrodene (M_1) styrene copolymerizations (▲) M_1^0:M_2^0 = 28.7:71.3; (■) M_1^0:M_2^0 = 48.4:51.6; (●) M_1^0:M_2^0 = 69.9:30.1; (♦) M_1^0:M_2^0 = 83.1:16.9.

Only small amounts of 2 were available. Thus, the disappearance of monomers was followed, quantitatively, by GLC using internal standards and electronic integration techniques. In this way, the incorporation of monomers into the copolymer could be followed as a function of percent conversion. Several composition–conversion data points could be obtained for each individual experiment, allowing large numbers of points to be achieved with minimum expenditure of monomer. The composition–conversion data obtained when styrene was M_2 are summarized in Table I and Figure 1. These data were fitted to the *integrated* form of the copolymer equation by the *nonlinear-least-squares* method of Tidwell and Mortimer[23,24] using programs we prepared for use on a Univac 1110 computer.[25] In addition to using the nonlinear fitting technique, M_1^0:M_2^0 ratios were applied in the vicinity of the *optimum values* for the reactivity ratios obtained. The importance of this choice of experiments has been discussed by Tidwell and Mortimer.[23,24]

From the data in Table I, the value of $r_1 = 0.30$ (0.287–0.313) and $r_2 = 0.82$ (0.774–0.875) (where M_2 = styrene). Using the relationship $r_1r_2 = \exp[-(e_1 - e_2)^2]$,[18,19] the Price e value for vinylcynichrodene is −1.98. This may be compared to e values of −2.1 and −1.99 for vinylferrocene and vinylcymantrene, respectively, in copolymerizations with styrene. Clearly, vinylcynichrodene is exceptionally electron rich and its reactivity closely resembles that of vinylcymantrene.

In order to appreciate just what this high negative value of *e* means, it is instructive to consider the *e* values for selected monomers:[19] maleic anhydride, +2.25; acrylonitrile, +1.20; styrene, −0.80; *p*-*N*,*N*-dimethylaminostyrene, −1.37; and 1,1-bis(*p*-anisyl)ethylene, −1.96. Quite obviously, the electron-rich vinylcynichrodene (−1.98) might be expected to undergo cationic polymerization while resisting anionic polymerization. Indeed, reaction with BuLi or $LiAlH_4$ failed to give polymer, supporting this conclusion.

The value of the resonance parameter *Q* for vinylcynichrodene, from these styrene copolymerizations, was 3.13.



Q 1.36 1.00 1.63 2.86 0.002 3.13

This may be compared to the monomers shown below.[19] Clearly, a strong resonance interaction of the vinyl group with the cyclopentadienyl ring is indicated. It is particularly noteworthy to recognize the similarity in the values of *Q* for 2-vinylthiophene (2.86) and vinylcynichrodene (3.13). In both these monomers the vinyl group is conjugated to an aromatic five-membered ring. However, the electron-donating ability of the $(\eta^5\text{-}C_5H_4)Cr(CO)_2NO$ substituent ($e = -1.98$) is substantially greater than that of the 2-thiophenyl group ($e = -0.80$).

Table II
Composition–Conversion Data for Copolymerizations of Vinylcynichrodene, 2, with *N*-Vinyl-2-pyrrolidone (M_2)[a]

Run	Vinylcynichrodene in feed, mol %	Conversion, %	Vinylcynichrodene in copolymer, mol %
1a	5.44	2.56	32.7
1b	5.44	10.82	36.8
1c	5.44	13.32	28.6
1d	5.44	13.72	30.1
1e	5.44	13.14	30.0
1f	5.44	14.02	28.0
1g	5.44	17.22	23.8
1h	5.44	20.65	24.5
1i	5.44	43.32	10.2
2a	22.36	3.13	64.8
2b	22.36	3.12	68.6
2c	22.36	6.41	69.0
2d	22.36	6.85	69.6
2e	22.36	7.23	65.7
2f	22.36	7.18	68.6
2g	22.36	7.55	67.3
2h	22.36	10.92	62.5
2i	22.36	11.12	66.5
2j	22.36	11.48	65.9
3a	3.33	9.79	21.9
3b	3.33	10.36	20.4
3c	3.33	10.12	20.8
3d	3.33	10.11	21.2
3e	3.33	9.88	21.3
3f	3.33	10.70	19.4
3g	3.33	10.91	18.5
4a	27.87	2.14	68.0
4b	27.87	5.66	67.0
4c	27.87	6.04	69.6
4d	27.87	6.40	69.5
4e	27.87	6.39	71.1
4f	27.87	6.55	69.9
4g	27.87	6.77	68.9
4h	27.87	6.62	68.7
4i	27.87	7.09	70.0

[a] From these data the calculated reactivity ratios are $r_1 = 5.34$ and $r_2 = 0.079$.

Table III
Composition–Conversion Data for Copolymerizations of Vinylcynichrodene, 2, with Vinylcymantrene

Vinylcynichrodene in feed, mol %	Conversion, %	Vinylcynichrodene in copolymer, mol %
30.84	7.5	34.5
30.84	9.3	35.3
30.84	9.9	35.4
30.84	10.4	35.0
30.84	10.8	35.1
30.84	10.5	34.7
30.84	10.6	35.3
30.84	17.0	34.6
30.84	20.1	34.5
30.84	21.8	35.7
30.84	21.5	34.8
30.84	21.5	35.1
30.84	21.5	34.9

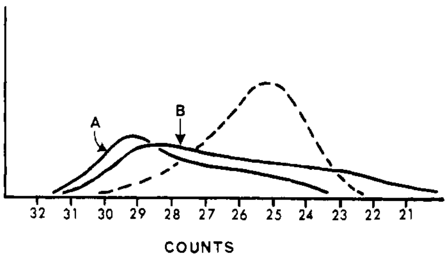


Figure 2. Gel permeation chromatograms of vinylcynichrodene polymers: (—) (A) polyvinylcynichrodene, bulk polymerization at 100 °C, with AIBN initiator; and (B) polyvinylcynichrodene, polymerized in ethyl acetate to 6.4% conversion using AIBN initiator; (- - -) copolymer of vinylcynichrodene and *N*-vinylpyrrolidone (No. 1i, Table II).

Reactivity studies were also performed with *N*-vinyl-2-pyrrolidone (M_2). This monomer was chosen because it has a somewhat more electron rich vinyl group ($e = -1.14$) than styrene ($e = -0.80$) and a much smaller value of *Q* (0.14 vs. 1.00 for styrene). It was of interest to check if *Q*–*e* studies based on copolymerizations with *N*-vinyl-2-pyrrolidone would give an *e* value for vinylcynichrodene close to that obtained in **2**/styrene copolymerizations. Composition–conversion studies, obtained in the same manner as in the **2**/styrene copolymerizations, are listed in Table II. Using the nonlinear-least-squares technique, the reactivity ratios were $r_1 = 5.34$ (5.08–5.60) and $r_2 = 0.079$ (0.073–0.084) and $e_1 = -2.07$. The agreement between the values of *e* in copolymerizations of **2** with styrene and *N*-vinyl-2-pyrrolidone (i.e., −1.98 and −2.07) is remarkable and strengthens the assignment of *e* at about −2.

Vinylcymantrene was copolymerized with vinylcynichrodene but only a single M_1^0:M_2^0 ratio was employed. Thus, the reactivity ratios were not calculated. These data are given in Table III.

Homopolymerizations. Radical-initiated homopolymerizations of vinylcynichrodene were rather slow but good yields could be achieved in ethyl acetate using azo initiators. Only an 11% yield was isolated when neat vinylcynichrodene was heated to 100 °C in the presence of AIBN for 2 h followed by sequential initiator addition and heating 3 h more at 100 °C. These results are similar to those found in solution polymerizations of vinylferrocene where low yields were always obtained unless multiple initiator additions were made.[26]

Since the homopolymerization of vinylferrocene has been carefully studied,[26–28] it was worthwhile to look for similarities

Table IV
Homopolymerization of Vinylcynichrodene in Ethyl Acetate Initiated by AIBN at 70 °C [a]

Run	2 charged, g	AIBN, g	Ethyl acetate, g	[2], mol/L	[2]/[AIBN]	Polymer yield, %	$\overline{M}_n$	$\overline{M}_w$
1	1.0274	0.0024	1.838	2.18	307	36	18 900	23 100
2	1.0052	0.0796	1.828	2.01	9	90	12 060	13 900
3	1.0012	0.0194	1.791	2.14	37	79	13 600	15 900
4	0.5106	0.0096	0.235	7.95	38	95	18 500	23 600
5	0.7855	0.0158	5.780	0.53	31	42	10 800	11 500

[a] All reactions were carried out for 20 h.

Table V
Results of the Fractionation of Poly(vinylcynichrodene)

Fraction no.[a]	Elution vol[b]	Mol wt[c]
1	23.61	30 000
2	24.79	20 740
3	26.40	13 540
4	28.05	8 800
5	28.68	7 000

[a] These are selected fractions from the GPC fractionation of the polymer produced in run 2, Table IV. [b] At 5 mL/count. [c] Peak average molecular weights determined by ultracentrifugation using the sedimentation equilibrium method.

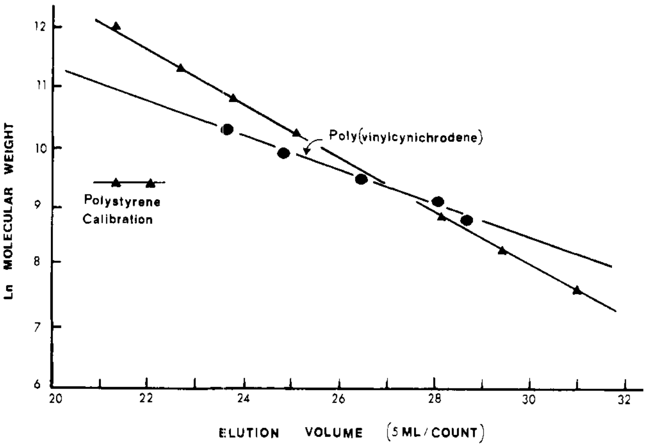


Figure 3. GPC calibration of the poly(vinylcynichrodene) fractions list in Table V vs. the "adjusted" polystyrene calibration.

between vinylferrocene and vinylcynichrodene in preliminary homopolymerization studies of the latter. The molecular weight of polyvinylferrocene did not increase when the initiator concentration or the [M]/[I] ratio was increased.[26] This was the result of a monomolecular termination mechanism which requires DP = $k_p[M]/k_t$.[27,28] Furthermore, as the degree of polymerization of polyvinylferrocene increased, its solubility decreased due to ionic site clustering which was the result of internal redox reactions occurring during monomolecular termination.[29] The magnitude of chain transfer to monomer ($C_m = 8 \times 10^{-3}$) was also large for vinylferrocene.[28]

Polyvinylcynichrodene appears to be highly branched when prepared in bulk. For example, its gel permeation chromatograms, of samples prepared in bulk, show broad molecular weight distributions with shoulders often occurring at the high molecular weight end (see Figure 2). These chromatograms resemble those of polyvinylferrocene prepared in bulk.

Due to the limited amount of available monomer, detailed kinetic studies could not be performed. Therefore, five homopolymerizations were carried out in ethyl acetate at 70 °C to examine the dependence of molecular weight on the [M]/[I] ratio (see Table III). Runs 1–3 held the monomer concentration constant at different initiator concentrations. Runs 3–5 held the [M]/[I] ratio constant at different monomer concentrations. The resulting polymers were analyzed by GPC and their molecular weights are summarized in Table IV.

The polymer from run 2 was fractionated into 23 microfractions by GPC and the molecular weights of five of these microfractions were obtained by ultracentrifugation using the sedimentation equilibrium method.[30] These values, summarized in Table V, were used to construct a GPC calibration plot for poly(vinylcynichrodene). This plot (Figure 3) of the ln of the molecular weights vs. elution volume was a straight line. From this plot it was possible to determine, accurately, the molecular weights of polymers 1–5 in Table IV without relying on secondary standards or the universal calibration method. As the [M]/[I] ratio was varied from 307 to 37 to 9, the values of $\overline{M}_n$ decreased from 18 900 to 13 600 to 12 060, respectively. The molecular weight also increased as the monomer concentration increased at constant [M]/[I]. The increase in molecular weight with an increase in [M]/[I] ratio indicates that vinylcynichrodene homopolymerizations, unlike those of vinylferrocene, are unlikely to be first order in initiator concentration.

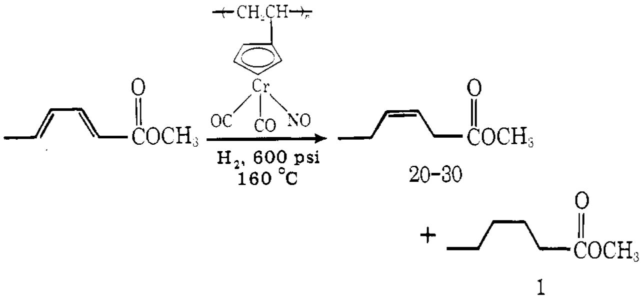
Recently, we have demonstrated that vinylcymantrene, **1**, homopolymerizations are half-order in initiator and three-halves order in monomer.[31] The close analogy between **1** and **2** suggests this kinetic equation should be considered in the homopolymerization of **2**. Therefore, the polymer yields for vinylcynichrodene homopolymerizations were predicted using both eq 1 and 2 below. The yields were predicted by numerical integration of the equations at 1-min intervals for 1200 min using 0.0024 min^{-1} as the rate constant for AIBN decomposition.[32] The rate constants for eq 1 and 2 were chosen to give a best fit to the experimental data for polymerization run 3 (Table V). The results show that eq 2 predicts the data for all the runs extremely well (better than eq 1).[33] While a regular rate study is clearly needed to draw firm conclusions, these initial studies suggest that the homopolymerization of **2** in ethyl acetate is half-order in initiator and first-order in monomer.

$$r_p = 1.758 \times 10^{-4}[\text{AIBN}]^{1/2}[2]^{3/2} \tag{1}$$

$$r_p = 1.70 \times 10^{-4}[\text{AIBN}]^{1/2}[2]^{1} \tag{2}$$

The calibration plot for poly(vinylcynichrodene) is compared to the polystyrene calibration in Figure 3.[34] The poly(vinylcynichrodene) calibration has a smaller slope than that for polystyrene. This illustrates that poly(vinylcynichrodene) is more rigid, a fact that was expected since the bulky organometallic group should reduce the flexibility of the polymer relative to a phenyl ring. Rigid polymers elute faster than flexible polymers of the same degree of polymerization (above a critical molecular weight) because they have a larger root mean square end to end distance and will not enter the gel pores as readily.

Catalytic Activity. Additional copolymerization studies are underway with a view toward obtaining polymers with novel properties. In this regard, cynichrodene, **3**, and several of its derivatives have been shown to catalyze hydrogenation.[35] Indeed, cynichrodene, **3**, poly(vinylcynichrodene), and its styrene copolymers catalyzed the selective 1,4-hydrogenation of methyl sorbate at 150–180 °C and 150–800 psi of hydrogen (eq 3). Thus, this complex resembles η^6-benzenetricarbonylchromium in its ability to effect the selective 1,4-hydrogenation of conjugated dienes.[36,37] Neither **3** nor its polymers would catalyze the hydrogenation of terminal or internal olefins. The mechanism of hydrogenation may only involve the loss of only one carbon monoxide from chromium since the nitrosyl ligand can shuttle between being a three- or one-electron donor.



Based on recent studies of Alt and Herbenhold,[38,39] the possibility of preparing chiral derivatives of **3** (or its polymers) is suggested. It would be very interesting to test a chiral derivative of cynichrodene as a asymmetric hydrogenation catalyst for 1,4-hydrogenations of conjugated dienes.

Experimental Section

All operations were carried out under nitrogen using Schlenk tube techniques. Hexane, benzene, and methylene chloride were purified by distillation from calcium hydride under nitrogen. Ethyl ether was predried over sodium wire and then distilled under nitrogen from sodium/benzophene. Merck silica gel was used for column chromatography. *N*-Vinylpyrrolidene and styrene were vacuum distilled from calcium hydride and vinylcymantrene was vacuum distilled using a short column. From GLC its purity was at least 99.5% Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. NMR and IR spectra were recorded on Varian A-60 and Beckman IR-10 spectrometers, respectively.

Vinylcynichrodene (2). This was prepared as described[22] as a red liquid: bp 79–80 (0.3 mmHg); 0.41 g (86%); IR (neat) 1952, 2030 (CO), 1700 cm^{-1} (NO); ^{1}H NMR ($CDCl_3$) δ 3.5–4.9 (m, ABC, vinyl), 4.85 (m, $H_{2,5}$), 5.08 (t, $H_{3,4}$). Anal. Calcd for $C_9H_7CrNO_3$: C, 47.17; H, 3.08; Cr, 22.69; N, 6.11. Found: C, 47.41; H, 3.10; Cr, 22.46; N, 6.36.

Homopolymerization. Vinylcynichrodene (1.072 g, 4.6 mmol), AIBN (0.0024 g, 0.15 mmol), and ethyl acetate (1.45 g) were weighed into a vial which was degassed by two freeze–thaw–pump cycles. The vial was sealed and placed in a constant temperature bath at 70 °C for 49 h. The ethyl acetate solution was then added dropwise to a large excess (50 mL) of pentane to precipitate the polymer. The precipitated homopolymer was filtered and dried in vacuo, to give 0.069 g (6.4% yield) of polyvinylcynichrodene. The IR of the polymer contains carbonyl stretching bands at 2020 and 1930 cm^{-1} and a nitrosyl stretch at 1680 cm^{-1}. In another run, neat vinylcynichrodene (0.5 g) was mixed with AIBN (5 mg) followed by heating to 100 °C for 2 h followed by the addition of another 5 mg of AIBN. After an additional 3 h methanol (2 mL) was added and the precipitated polymer was washed with excess methanol and dried giving 56 mg (11%) yield of polyvinylcynichrodene. Gel permeation chromatography of this sample revealed a broad molecular weight distribution with a low $\overline{M}_n$.

Copolymerizations. All copolymerizations were performed in dried, deoxygenated benzene at 70 °C in 3-mL minivert sample vials stirred magnetically. In each case, the disappearance of the monomers was followed by GLC. A typical run is described for one vinylcynichrodene/styrene copolymerization. Vinylcynichrodene, styrene, napthalene (used as an internal GLC standard), and benzene were weighed into a 3-mL vial. A small aliquot was removed into a 1-mL vial. Then both vials were degassed under nitrogen by five freeze–flush–thaw cycles. The initiator, 33W (i.e., 2,2′-azobis(2,4-dimethyl-4-methoxyvaleronitrile)), was added by syringe (in benzene solution) several times during the polymerization. At least 1 h was allowed after each initiator injection before sampling the reaction for GLC analysis. In some reactions, AIBN was used as the initiator and in these cases it was added prior to degassing. The same procedure was used when the comonomer was *N*-vinylpyrrolidone or vinylcymantrene.

Analysis of Copolymerization Reactions. A typical example is described for a styrene copolymerization. The analysis of monomer remaining in the reaction as a function of time was carried out by GLC (1/8 in. × 50 cm, OV-101 (5%) on Chromasorb G-HP, 100/120 mesh, flow rate 22 cm^3 min^{-1}, injection 80 °C, detector 160 °C, filament 170 °C, temperature-programmed 1 min at 45 °C, 5 °C min^{-1} to 110 °C, 6 min at 110 °C). Several injections were made into the column prior to gathering data. A Varian Associates Model 3700 gas chromatograph was used and electronic integration was performed using a Hewlett-Packard Model 3380A recorder-integrator.

Samples from the 1-mL reference vial were alternately injected with samples from the polymerizing solution, which were withdrawn from the 3-mL vial being held at constant temperature in a water bath. Three injections were averaged to determine the amount of each monomer remaining as a function of time. The internal standards used included quinoline (for *N*-vinylpyrrolidone copolymerizations) and napthalene (for both styrene and vinylcymantrene copolymerizations).

Catalytic Hydrogenation of Methyl Sorbate. Methyl sorbate (1.5 g, 11.9 mmol) was dissolved in 200 mL of pentane and cynichrodene (0.2 g, 0.98 mmol) was added. The resulting solution was added to a 1-L autoclave. The autoclave was thoroughly flushed with hydrogen to remove all of the air that was in it, pressurized with 200 psi of hydrogen, and then heated to 160 °C to give a pressure of 550 psi. The reaction was stirred under this condition for 5 h and then cooled. The solution was allowed to cool and then was filtered. The pentane was removed under vacuum to give a mixture of methyl sorbate (7.96 mmol, 67%), (*Z*)-(methyl 3-hexenoate) (3.81 mmol, 32%), and methyl hexanoate (0.12 mmol, 1%). The products were separated by prep GLC and identified as previously described.[37]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (MDR), to the National Science Foundation Grant No. DMR77-06810 Polymers Program, and to the Office of Naval Research (CUP) for support of this research.

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Calculated γ Effects on the ^{13}C-NMR Spectra of 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers and Their Implications for the Conformational Characteristics of Polypropylene

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ABSTRACT: The Suter–Flory rotational isomeric state (RIS) model of polypropylene is employed to calculate the ^{13}C-NMR chemical shifts expected at the 9-C$^{\alpha}$ and CH$_3$ carbons and at the 8- and 10-CH$_2$ carbons in the various stereoisomers of the polypropylene model compound 3,5,7,9,11,13,15-heptamethylheptadecane (I). Differences in the chemical shifts of the same carbon atom in the various stereoisomers are assumed to be attributable solely to stereosequence-dependent differences in the probability that the given carbon atom is involved in three-bond gauche or γ interactions with other carbon atoms. When this approach is followed with a γ effect of −5.3 ppm for each three-bond gauche C---C interaction, the observed ^{13}C-NMR spectrum of the central 9-CH$_3$ carbon atom in I, including temperature effects, can be fully explained in terms of the possible stereoenvironments. Consequently, the Suter–Flory RIS model appears to provide an accurate description of the conformational characteristics of polypropylene which permits a detailed understanding of its ^{13}C-NMR spectrum.

^{13}C-NMR spectroscopy[1,2] is currently the most powerful experimental probe used to determine the stereoconfiguration and/or sequence distribution of monomer units constituting vinyl homo- and copolymers. The connections between the stereosequences and ^{13}C-NMR spectra have been drawn[1] numerous times for many different vinyl polymers. However, it was only recently suggested[3,4] that the observed stereochemical shifts in the ^{13}C resonance peaks could be attributed to conformational differences among the various stereosequences.

It is apparent from ^{13}C-NMR studies[4-7] of paraffinic hydrocarbons (see Figure 1a) that the gauche arrangement of carbon atoms separated by three bonds (γ substituents) results in an upfield shift (γ effect) relative to the shielding experienced in the trans planar conformation (see Figure 1b). Clearly the magnitude of the γ effect experienced by a given carbon atom in a vinyl polymer chain should depend on the proportion or probability of those bond conformations which produce a gauche arrangement between the carbon atom of interest and those carbon atoms attached in the γ position.

The probability that any given bond in the vinyl polymer adopts a particular rotational state is known[8,9] to be sensitive to the stereosequence of the chain in the vicinity of the bond in question. It is therefore reasonable to expect the ^{13}C chemical shift pattern observed for a vinyl polymer to be directly related to its conformational characteristics as determined by the stereosequence of the chain.

Bovey[4] was able to approximate the triad structure in the ^{13}C-NMR methyl spectrum of atactic polypropylene by estimating[10] the number of methyl carbon gauche interactions present in each triad and assigning each a γ effect of −4.3 ppm. More recently Provasoli and Ferro[11] have attempted to calculate the chemical shifts of the central (9) methyl carbon in the stereoisomers of 3,5,7,9,11,13,15-heptamethylheptadecane (I), a model compound[12,13] for polypropylene.

In addition to the γ effect, whose magnitude was least-squares fitted to the observed chemical shifts, the latter authors also considered the deshielding effect of a carbon atom separated by four bonds (δ substitution) in the syn-axial arrangement with respect to the observed carbon atom (see Figure 1c). They assigned the δ effect a value of 3 ppm and determined the probabilities of finding bond pairs on either side of C$_9{}^{\alpha}$ in the syn-axial conformation for each of the stereoisomers of I. The three-state [trans (t), gauche$^+$ (g), and gauche$^-$ ($\bar{\text{g}}$)] rotational isomeric state (RIS) model for polypropylene developed by Boyd and Breitling[14] was used to

0024-9297/78/2211-0565$01.00/0