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THE VINYL REACTIVITY OF (ETA (5)-VINYLCYCLOPENTADIENYL)
MAY 78 C U PITTMAN, T D ROUNSEFELL, E A LEWIS N00014-75-C-0689
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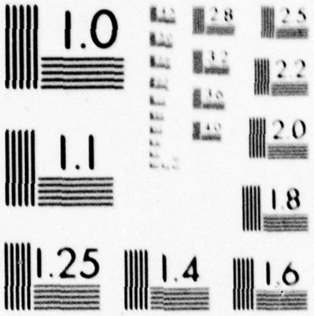
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The novel vinyl organometallic monomer (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (hereafter called vinylcynichrodene)**, 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.*** 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 eval-

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uated 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 trivial name cynichrodene is proposed by analogy to the shortened names cymantrene and benchrotrene for η^5-cyclopentadienyltricarbonylmanganese and η^6-benzenetricarbonylchromium, respectively.

***N-vinyl-2-pyrrolidone is also known as N-vinyl-2-pyrrolidinone.

OFFICE OF NAVAL RESEARCH
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TECHNICAL REPORT NO. 21

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

by

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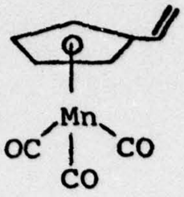
INTRODUCTION

The synthesis of organometallic polymers[1-5] and studies of their novel properties[1-7] 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] <u>1</u>, is isoelectric with vinylcynichrodene, <u>2</u>. 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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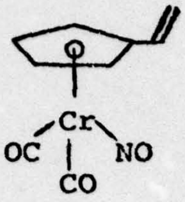

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We now report the addition homopolymerization and copolymerization of the novel monomer, vinylcynichrodene, 2. To our knowledge, this represents the first example of the polymerization of an organometallic monomer containing a nitrosyl (NO) substituent. Furthermore, we demonstrate that changing the metallic fragment from Mn$(CO)_3$ to Cr$(CO)_2$NO 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[1-3,8-17] 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°/0.3 mm Hg, 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). 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 2). Azo initiators were used in each case. A series of copolymerizations with styrene were carried out to determine the reactivity

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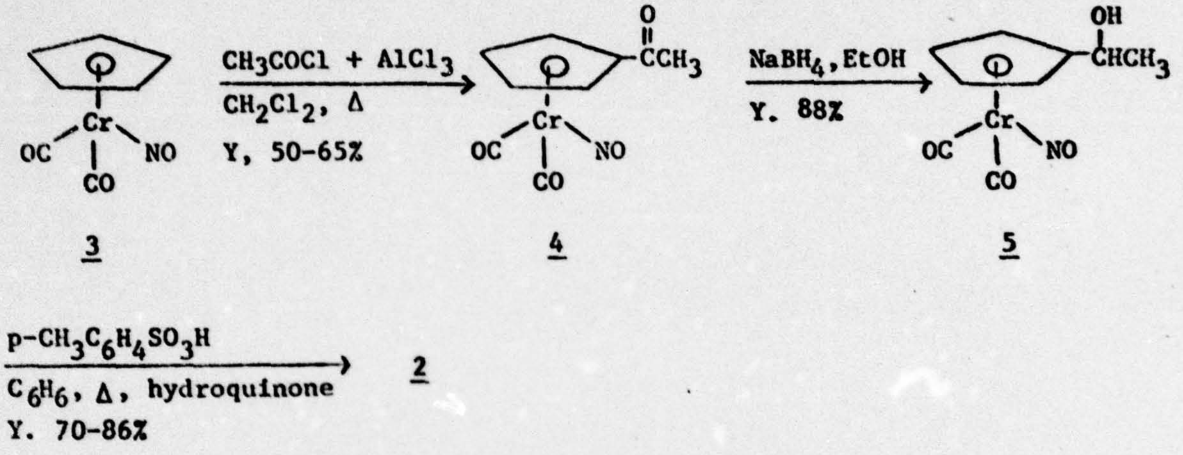
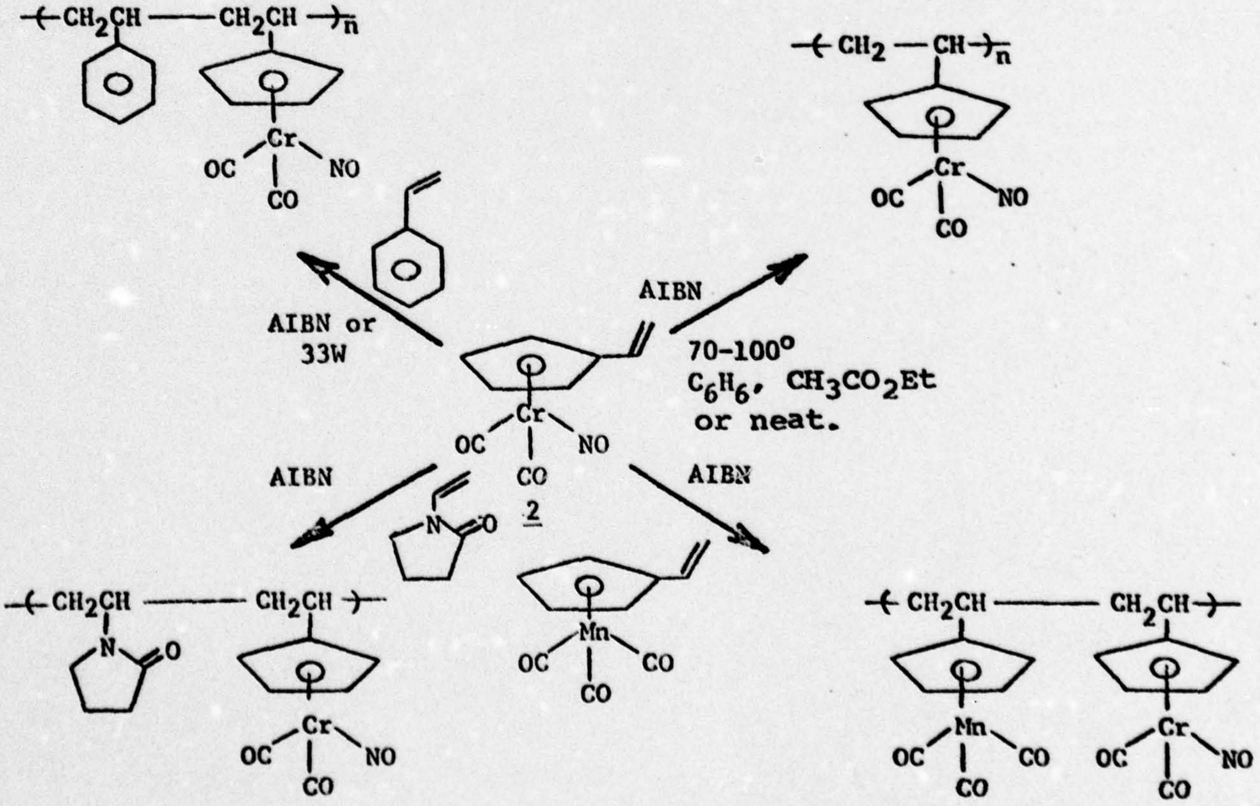
Scheme I.



Scheme II.



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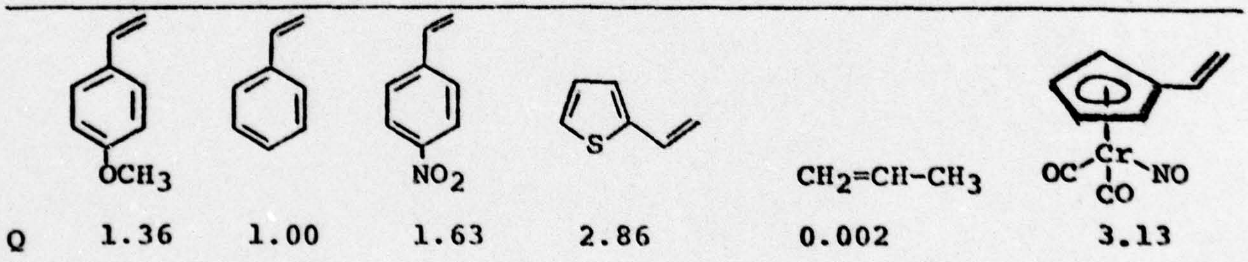
ratios of 2. Styrene was chosen because it had previously been used in reactivity ratio studies with vinylferrocene and vinylcymantrene, 1.[1,17] Furthermore, styrene is a moderately electron rich monomer (e = -.80). We anticipated that if 2 were a very electron rich monomer, resembling 1, the use of electron attracting comonomers (i.e., acrylonitrile or methyl acrylate) might result in failure of the Q-e scheme, similar to that observed for both vinylferrocene and 1 when copolymerized with electron attracting monomers.[17]

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 is summarized in Table 1 and Figure 1. This data was 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, $M_1^o:M_2^o$ 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 1, 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. 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 = -.80).

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 = -.80) and a much smaller value of Q (0.14 versus 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 2. 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 $M_1^o:M_2^o$ ratio was employed. Thus, the reactivity ratios were not calculated. This data is given in Table 3.

Homopolymerizations

Radical-initated 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° in the presence of AIBN for two hours followed by sequential initiator addition and heating three more hours at 100°. 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 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° to examine the dependence of molecular weight on the [M]/[I] ratio (see Table 4). 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 4.

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 5, were used to construct a GPC calibration plot for poly(vinylcynichrodene). This plot (Figure 3) of the ln of the molecular weights versus elution volume was a straight line. From this plot it was possible to determine, accurately, the molecular weights of polymers 1-5 in Table 4 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 $\bar{M}_n$ 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, <u>1</u>, 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 equations 1 and 2 below. The yields were predicted by numerical integration of the equations at one minute intervals for 1200 minutes using 0.0024 min.^{-1} as the rate constant for AIBN decomposition.[32] The rate constants for equations 1 and 2 were chosen to give a best fit to the experimental data for polymerization run 3 (Table 5). The results show that equation 2 predicts the data for all the runs extremely well (better than equation 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.

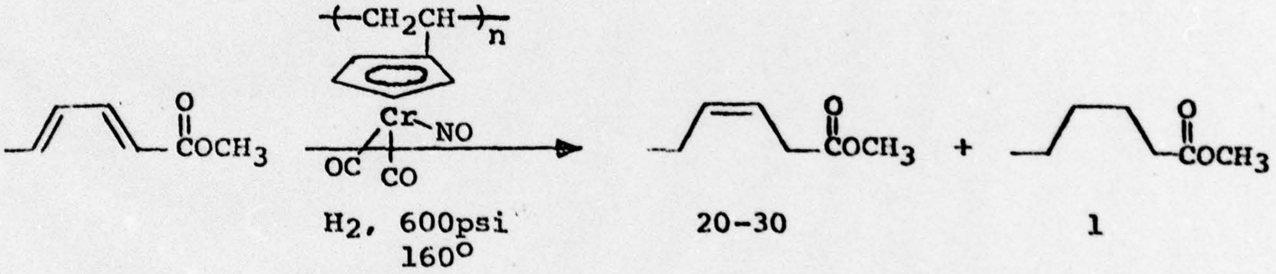
$$r_p = 1.758 \times 10^{-4}[\text{AIBN}]^{1/2}[\underline{2}]^{3/2} \qquad (1)$$

$$r_p = 1.70 \times 10^{-4}[\text{AIBN}]^{1/2}[\underline{2}]^{1} \qquad (2)$$

The calibration plot for poly(vinylcynichrodene) is compared to the polystyrene calibration in Figure 3.[34] The poly(vinylcynichrodene) calibration occurs above that for polystyrene, and it has a smaller slope. 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 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° and 150-800 psi of hydrogen (equation 3). Thus, this complex resembles



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η⁶-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

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 pre-dried 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 79-80/0.3mm Hg; 0.41 g (86%). IR (neat): ν(CO) 1952, 2030 cm^{-1}; ν(NO) 1700 cm^{-1}; PMR ($CDCl_3$): δ3.5-4.9, m(ABC), vinyl: 4.85, m, $H_{2,5}$; 5.08, t, $H_{3,4}$; $C_9H_7CrNO_3$ calcd: 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° fcr 49h. 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 <u>in vacuo</u>, 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° for 2h followed by the addition of another 5 mg of AIBN. After an additional 3h, methanol (2 ml) was added, 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° in 3ml 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 one 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 one hour 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 ($^{1}/_{8}$" x 50 cm, OV-101 (5%) on Chromasorb G-HP, 100/120 mesh, flow rate 22 cc. min.$^{-1}$, injection 80°, detector 160°, filament 170°, temperature-programmed 1 min. at 45°, 5° min^{-1} to 110°, 6 min. at 110°). 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 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 1.5g (11.9mmol) was dissolved in 200ml of pentane and cynichrodene 0.2g (0.98mmol) added. The resulting solution was added to a 1 liter autoclave. The autoclave was thoroughly flushed with hydrogen to remove all of the air that was in it, and then pressurized with 200psi of hydrogen, and then heated to 160^{o} to give a pressure of 550psi. The reaction was stirred under this condition for 5hr., and then cooled. The solution was allowed to cool, and then filtered. The pentane was removed under vacuum to give a mixture of methyl sorbate (7.96mmol, 67%), Z-(methyl 3-hexenoate)(3.81mmol, 32%), and methyl hexanoate (0.12mmol, 1%). The products were separated by prep glc and identified as previously described.[37]

ACKNOWLEDGEMENT

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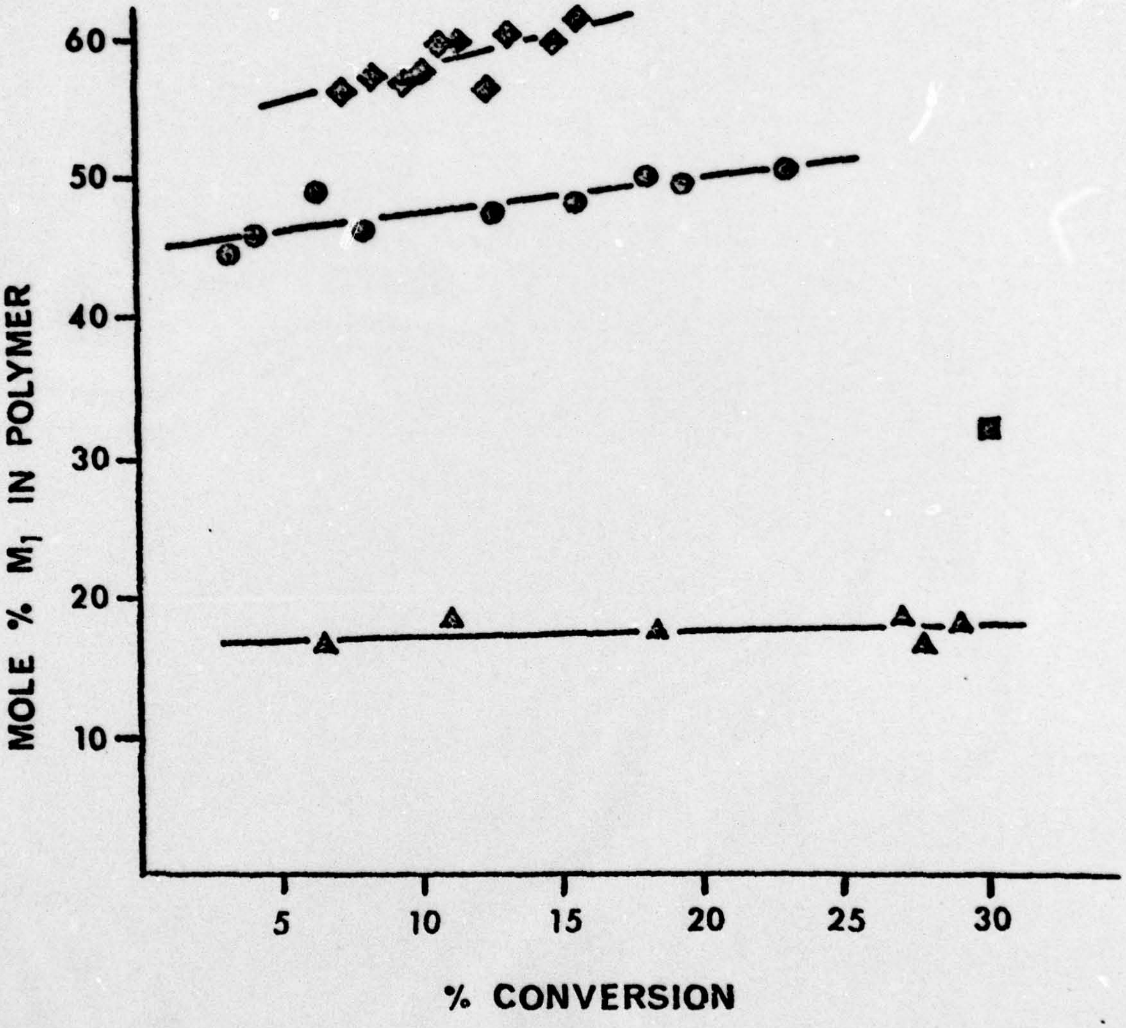
FIGURE 1. Composition-Conversion Plots for Example Vinylcynichrodene (M_1) Styrene Copolymerizations

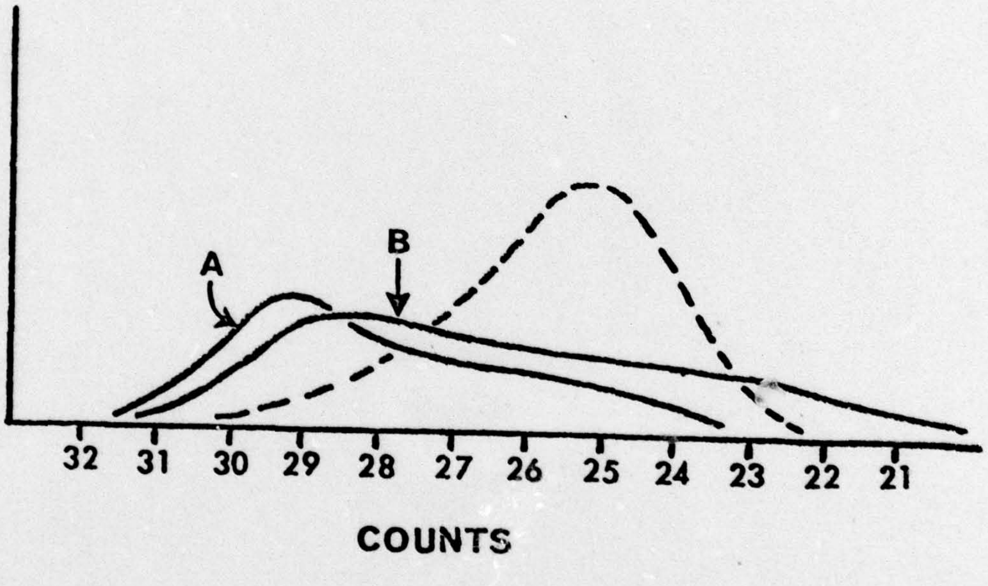
▲ $M_1^o:M_2^o = 71.3:28.7$
⊠ $M_1^o:M_2^o = 48.4:51.6$
◉ $M_1^o:M_2^o = 69.9:30.1$
◈ $M_1^o:M_2^o = 83.1:16.9$

FIGURE 2. Gel Permeation Chromatograms of Vinylcynichrodene Polymers

____A. Polyvinylcynichrodene. Bulk polymerization at 100°, with AIBN initiator.
____B. Polyvinylcynichrodene. Polymerized in ethyl acetate to 6.4% conversion using AIBN initiator.
----- Copolymer of Vinylcynichrodene and N-Vinylpyrrolidone (No. li, Table 2).

FIGURE 3. GPC Calibration of the Poly(vinylcynichrodene) Fractions List in Table 5 Versus the "Adjusted" Polystyrene Calibration


MOLE % M_1 IN POLYMER
60
50
40
30
20
10
5
10
15
20
25
30
% CONVERSION


A
B
32
31
30
29
28
27
26
25
24
23
22
21
COUNTS

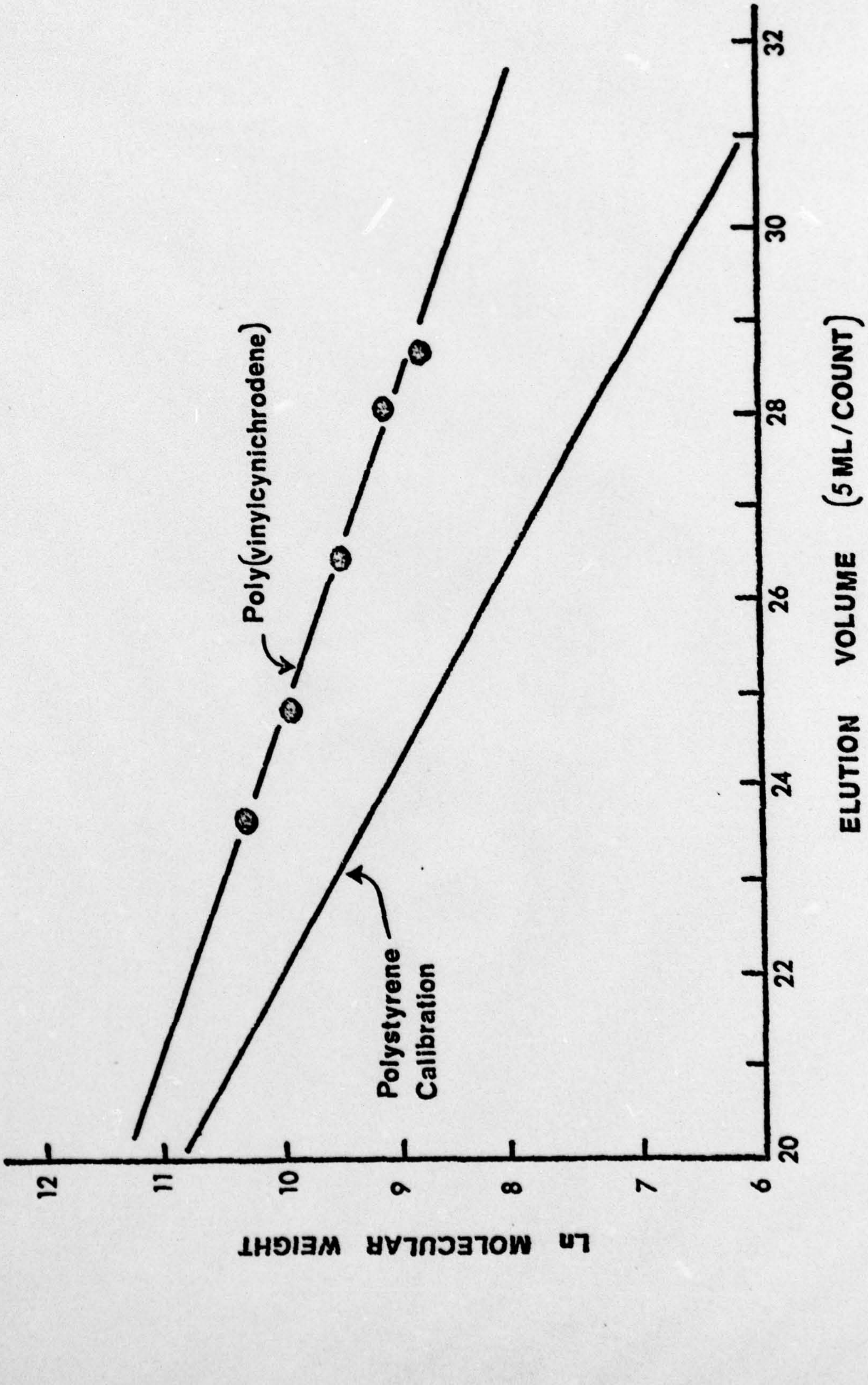

Ln MOLECULAR WEIGHT
12
11
10
9
8
7
6
20
22
24
26
28
30
32
ELUTION VOLUME (5 ML/COUNT)
Poly(vinylcynichrodene)
Polystyrene Calibration

TABLE 1

Composition-Conversion Data for Copolymerizations Vinylcynichrodene, 2, with Styrene (M_2)[a]

Run	Vinylcynichrodene in Feed Mole %	Conversion %	Vinylcynichrodene in Copolymer Mole %
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 this data the calculated reactivity ratios for this monomer pair are $r_1 = 0.30$ and $r_2 = 0.82$.

TABLE 2

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

Run	Vinylcynichrodene in Feed Mole %	Conversion %	Vinylcynichrodene in Copolymer Mole %
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 this data the calculated reactivity ratios are $r_1 = 5.34$ and $r_2 = 0.079$.

TABLE 3

Composition-Conversion Data for Copolymerizations of Vinylcynichrodene, 2, with Vinylcymantrene

Vinylcynichrodene in Feed Mole %	Conversion %	Vinylcynichrodene in Copolymer Mole %
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

TABLE 4. Homopolymerization of Vinylcynichrodene in Ethyl Acetate Initiated by AIBN at 70° [a]

Run	2 Charged g	AIBN g	Ethyl Acetate g	[2] Moles/l	[2]/[AIBN]	Polymer Yield %	$\bar{M}_n$	$\bar{M}_w$
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 5. Results of the Fractionation of Poly(vinylcynichrodene)

Fraction Number[a]	Elution Volume[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 5.

[b] At 5ml per count.

[c] Peak average molecular weights determined by ultracentrifugation using the sedimentation equilibrium method.

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