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THE PREPARATION, POLYMERIZATION AND COPOLYMERIZATION OF SUBSTIT--ETC(U)

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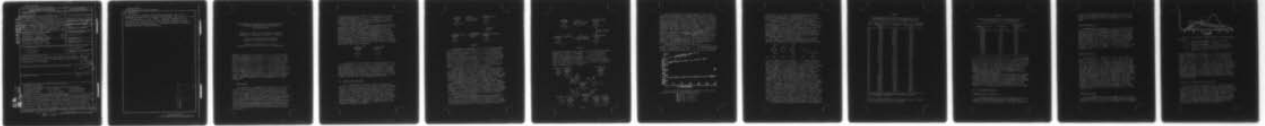
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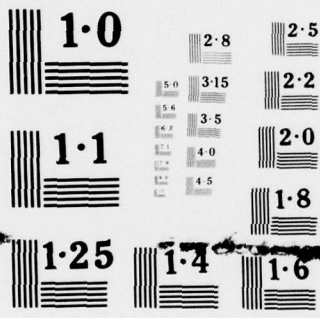
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20. ABSTRACT

-1.98 and the resonance interaction parameter Q was 3.1. Copolymerizations with N-vinyl-2-pyrrolidone (M_2) gave $r_1 = 5.3$, $r_2 = 0.079$ and $e = -2.07$. Thus, vinylcynichrodene is an exceptionally electron-rich vinyl monomer resembling vinylferrocene and vinylcymantrene. Vinylcynichrodene readily copolymerized with vinylcymantrene.

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THE PREPARATION, POLYMERIZATION AND COPOLYMERIZATION
OF SUBSTITUTED DERIVATIVES OF CYNICHRODENE
($\eta^5\text{-C}_5\text{H}_5$)Cr(CO)₂NO

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ABSTRACT. The novel vinyl organometallic monomer (η^5 -vinyl-cyclopentadienyl)dicarbonylnitrosylchromium (hereafter called vinylcynichrodene)*, was prepared and homopolymerized and copolymerized in solution and neat using azo initiators. 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 -1.98 and the resonance interaction parameter Q was 3.1 . Copolymerizations with *N*-vinyl-2-pyrrolidone (M_2) gave $r_1 = 5.3$, $r_2 = 0.079$ and $e = -2.07$. Thus, vinylcynichrodene is an exceptionally electron-rich vinyl monomer resembling vinylferrocene and vinylcymantrene. Vinylcynichrodene readily copolymerized with vinylcymantrene.

I. 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⁾

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

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ferrocenylmethyl acrylate, (12,13) η^6 -(2-phenylethyl acrylate)-tricarboxylchromium, (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)

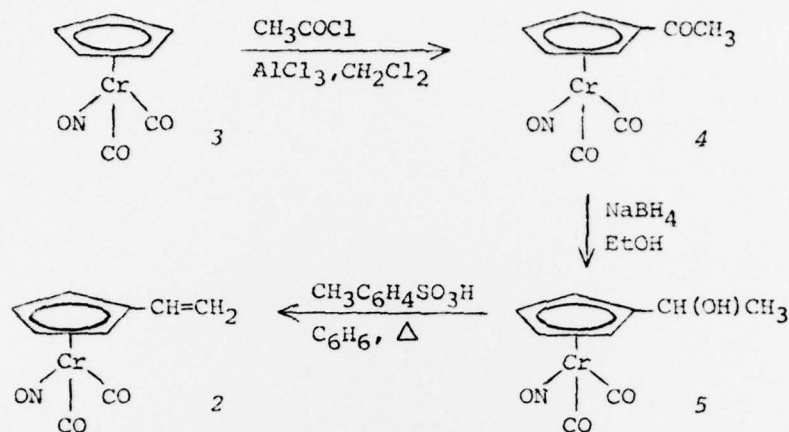
Addition polymerization studies of organometallic carbonyl monomers are rare, indeed, compared with metallocenes. (3) Organochromium monomer syntheses and polymerizations are restricted to the three examples: η^6 -styrenetricarbonylchromium, (3) η^6 -(benzyl acrylate)tricarboxylchromium, (11) and η^6 -(2-phenylethyl acrylate)tricarboxylchromium. (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.



We now report the addition of 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.

II. RESULTS AND DISCUSSION.

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 according to Scheme I.



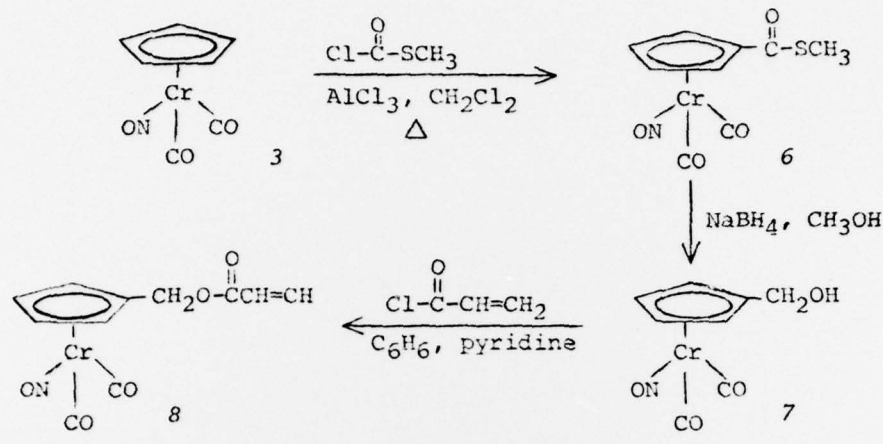
Scheme 1

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. Cynichrodene was acetylated in 50-55% yield, followed by sodium borohydride reduction of the carbonyl group (88%) and *p*-toluene-sulfonic acid-catalyzed dehydration (70-85%) 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. In addition, glc studies of 2 were made to monitor its purity.

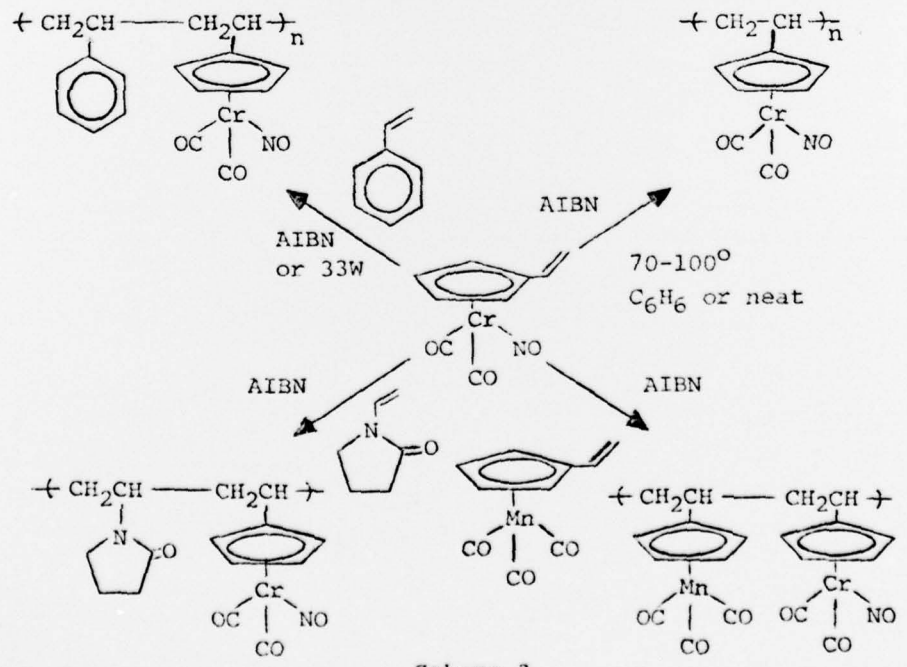
Cynichrodenylmethyl acrylate, 8, another useful organochromium monomer, is prepared as shown in Scheme II. Cynichrodene, 3, is converted to the thioester 6 under Friedel-Crafts conditions by means of methyl chlorothioformate and aluminum chloride in dry methylene chloride. Reduction of 6 with sodium borohydride in refluxing methanol gives cynichrodenylcarbinol, 7. Reaction of 7 with two equivalents of pyridine produces cynichrodenylmethyl acrylate, 8.

Vinylcynichrodene was homopolymerized and copolymerized with styrene, *N*-vinyl-2-pyrrolidone, and vinylcymantrene (Scheme 3). Azo initiators were used in each case. A series of copolymerizations with styrene were carried out to determine the reactivity ratios with 2. Styrene was chosen because it



Scheme 2

had previously been used in reactivity ratio studies with vinylcymantrene, 1. (1,17) Furthermore, styrene is a moderately electron rich monomer ($\rho = -.80$). We anticipated that if 2 were a very electron rich monomer resembling 1 the use of electron attracting comonomers (i.e., acetonitrile 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)



Scheme 3

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 on 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, $M_1^0:M_2^0$ 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 Figure 1, the value of $r_1 = 0.30$ (0.287 - 0.313) and $r_2 = 0.82$ (0.774 - 0.875) (where $M_2 = \text{styrene}$). Using the relationship $r_1 r_2 = \exp. -(\alpha_1 - \alpha_2)^2$ (18,19) the Price e -value for vinylcynichrodene is -1.98. This may be compared

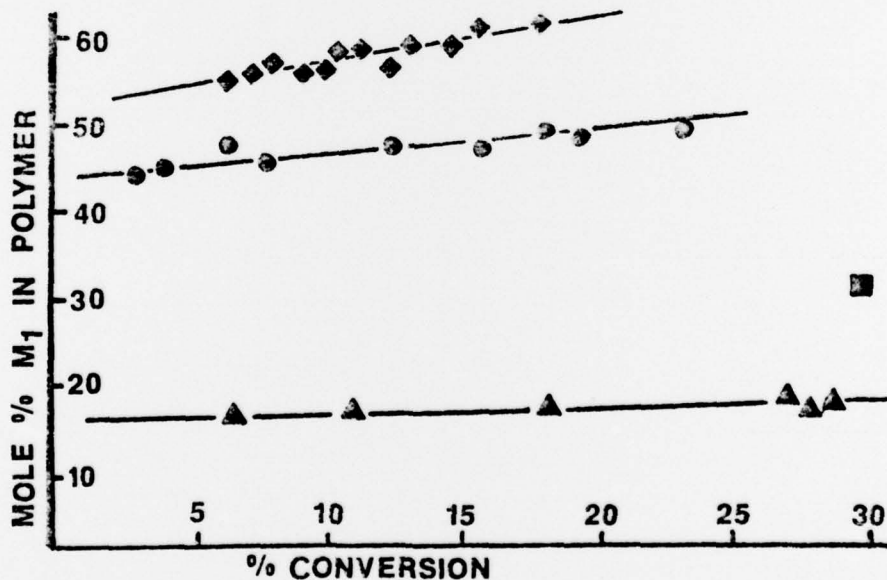


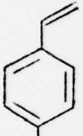
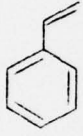
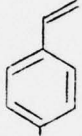
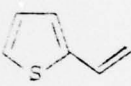
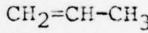
Fig. 1. Composition-conversion plots for example vinylcynichrodene (M_1) styrene copolymerizations.

- ▲ $M_1^0:M_2^0 = 71.3:28.7$
- $M_1^0:M_2^0 = 48.4:51.6$
- $M_1^0:M_2^0 = 69.9:30.1$
- ◆ $M_1^0:M_2^0 = 83.1:16.9$

to ρ -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 ρ means, it is instructive to consider the ρ -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) would be expected to undergo cationic polymerization while resisting anionic polymerization. Indeed, reaction with BuLi or LiAlH₄ 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,

					
Q	1.36	1.00	1.63	2.86	0.002

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, the vinyl group is conjugated to an aromatic five-membered ring. However, the electron-donating ability of the (η^5 -C₅H₄)Cr(CO)₂NO substituent (ρ = -1.98) is substantially greater than that of the 2-thiophenyl group (ρ = -.80).

Reactivity studies were also performed with *N*-vinyl-2-pyrrolidone (M₂). This monomer was chosen because it has a somewhat more electron rich vinyl group (ρ = -1.14) than styrene (ρ = -.80) and a much smaller value of Q (0.14 versus 1.00 for styrene). It was of interest to check if Q - ρ studies based on copolymerizations with *N*-vinyl-2-pyrrolidone would give an ρ -value for vinylcynichrodene close to that obtained in the styrene copolymerizations. Composition-conversion studies, obtained in the same manner as in the styrene copolymerizations, are listed in Table 1. 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 ρ_1 = -2.07. The agreement between the values of ρ 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 ρ at about -2.

Vinylcymantrene was copolymerized with vinylcynichrodene

TABLE 1

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

Run	Monomer <u>2</u> in Feed Mole %	Conversion %	Monomer <u>2</u> 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

* From this data the calculated reactivity ratios are
 $r_1 = 5.34$ and $r_2 = 0.079$.

but only a single $M_1^0:M_2^0$ ratio was employed (Table 2). Thus,
the reactivity ratios were not calculated.

TABLE 2

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

Monomer <u>2</u> in Feed Mole %	Conversion %	Monomer <u>2</u> 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	21.6	35.7
30.84	21.5	34.8
30.84	21.5	35.1
30.84	21.5	34.9

Radical initiated homopolymerizations of vinylcynichrodene were slow. Only a 6.4% yield of polymer was isolated after 49h at 70° in the ethylacetate using AIBN. Similarly, only an 11% yield was isolated when neat vinylcymantrene was heated to 100° (with AIBN) for 2h followed by further initiator addition and another 3h at 100°. Solution homopolymerizations give low molecular weights (below 35,000) and molecular weights increased when the monomer concentration increased or the initiator concentration decreased.

Additional copolymerization studies are currently underway involving 2 and other monomers with a view toward obtaining polymers with novel properties. In this regard, cynichrodene, 3, and several of its derivatives have been shown to effectively catalyze reactions such as hydrogenation.⁽²⁶⁾ Further, based on recent studies by Alt and Herberhold,^(27,28) the possibility of preparing chiral polymers is clearly available.

III. EXPERIMENTAL SECTION.

1-Hydroxyethylcynichrodene (5).

Acetylcynichrodene (2.2 g) (15) was dissolved in 25 ml of ethanol, 0.168 g of sodium borohydride was added, and the mixture was stirred for ca. 45 min. After this period, 10-20

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ml of 6N sodium hydroxide solution was added, the solvent removed, and the product extracted with ethyl ether. The ether was removed, leaving a red oil; bp 105-110°/0.3 mm Hg; 1.95 g (88%).

Vinylcynichrodene (2).

1-Hydroxyethylcynichrodene (0.5 g), 5 mg of hydroquinone, and 0.05 g of p-toluenesulfonic acid were dissolved in 50 ml of benzene, and the mixture refluxed for 1.25 h. The solvent was removed and the resulting oil was extracted with hexane and subsequently filtered through silica gel, eluting several times with hexane and then 5:1 hexane-ether. The solvent was removed leaving a red oil; bp 79-80°/0.3 mm Hg; 0.41 g (86%). Its IR spectrum gave strong ν_{CO} bands at 1952 and 2030 cm^{-1} and a ν_{NO} band at 1700 cm^{-1} . Its nmr was in accord with structure and its analysis found: C, 47.41; H, 3.10; Cr, 22.46; N, 6.36%. Calculated for $C_9H_7CrNO_2$: C, 47.17; H, 3.08; Cr, 22.69; N, 6.11.

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° for 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 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° 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 \bar{M}_n . (See Figure 2).

Copolymerizations.

All copolymerizations were performed in dried, deoxygenated benzene at 70° in a 3 ml minivert [®] sample vials stirred magnetically. In each case, the disappearance of the monomers

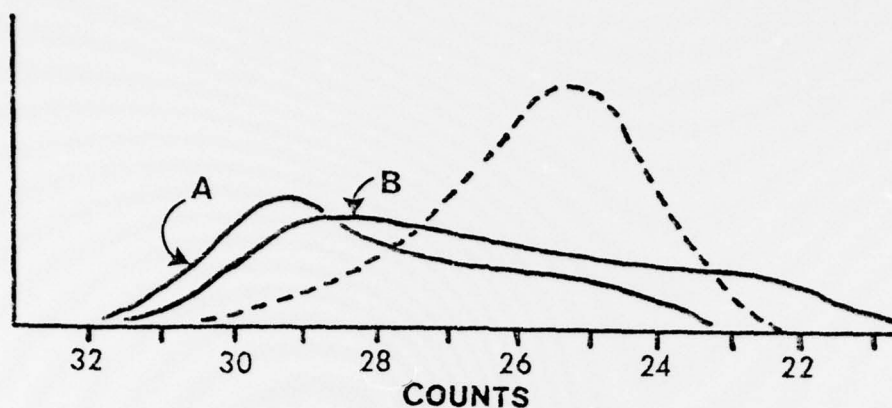


Fig. 2. Gel permeation chromatograms of vinylcynichrodene polymers.

- 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. 11, Table 1).

was followed by glc. A typical run is described for one vinylcynichrodene/styrene copolymerization. Vinylcynichrodene, styrene, naphthalene (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.

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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 naphthalene (for both styrene and vinylcymantrene copolymerizations). A sample gel permeation chromatogram is shown in Figure 2.

IV. ACKNOWLEDGEMENT.

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