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THE PREPARATION, POLYMERIZATION AND COPOLYMERIZATION OF (η^5-VINYLCYCLOPENTADIENYL)DICARBONYLNITROSYLCHROMIUM, (η^5-$C_5H_4CH{=}CH_2$)$Cr(CO)_2NO$

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Summary

The first report on the preparation, polymerization, and copolymerization of a nitrosyl-containing vinylcyclopentadienylmetal monomer, (η^5-$C_5H_4CH{=}CH_2$)-$Cr(CO)_2NO$, is described. (η^5-Vinylcyclopentadienyl)-dicarbonylnitrosylchromium (A) was prepared in good yield by the acylation of η^5-cyclopentadienylcarbonylnitrosylchromium followed by sodium borohydride reduction of the keto function and acid-catalyzed dehydration. Monomer A homopolymerizes and copolymerizes with styrene, *N*-vinylpyrrolidone, and vinyl cymantrene in the presence of azo initiators. Reactivity ratios in the copolymerization of A with styrene were $r_1 = 0.30$ and $r_2 = 0.82$ from which the value of e for A was found to be —1.98. Thus, A is an exceptionally electron-rich monomer.

Introduction

The synthesis of organometallic polymers [1—5] and studies of their novel properties [1,6,7] have accelerated greatly in scope in recent years. The radical-initiated vinyl addition, homopolymerization and copolymerization of a variety of organometallic monomers, such as η^6-styrenetricarbonylchromium [8], vinylcymantrene [1,9], vinylferrocene [10], η^6-(benzylacrylate)tricarbonylchromium [11], ferrocenylmethyl acrylate [12,13] and methacrylate [12,13], η^6-(2-phenylethyl acrylate)tricarbonylchromium [14], as well as 2-ferrocenylethyl acrylate [15] and methacrylate [15] have now been well-established.

Reports on the addition polymerization and copolymerization of organometal carbonyl monomers are rare in contrast to their metallocene analogs [3].

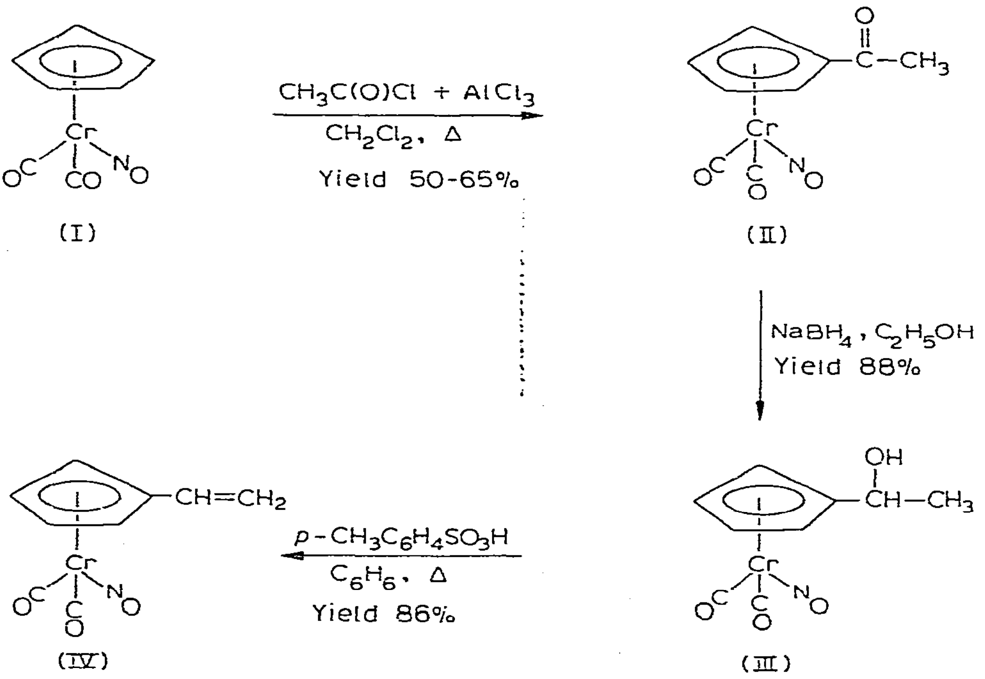
Furthermore, only a few organochromium monomers have been synthesized and polymerized. These include η^6-styrenetricarbonylchromium, η^6-(benzyl acrylate)tricarbonylchromium [11], and η^6-(2-phenylethyl acrylate)tricarbonylchromium [14].

We now report the first example of the synthesis, addition polymerization and copolymerization of an organochromium carbonyl nitrosyl monomer, namely, (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium(IV). To our knowledge, this also represents the first example of the polymerization of an organometallic monomer which contains a nitrosyl substituent.

Results and discussion

(η^5-Cyclopentadienyl)dicarbonylnitrosylchromium (I) was first prepared by Fischer et al. in 1955 [16]. Since that time the chemistry of this complex has remained relatively undeveloped. The complex has been acylated in good yield [17], but its ring-substitution chemistry remains largely unexplored. Pittman et al. [1—3,8—15,18] recently have published comprehensive studies of the addition polymerization reactivity of vinyl derivatives of organometallic complexes. It has been found that transition-metal organometallic functions, attached to a vinyl group, exert enormous effects on addition polymerization reactivity [18,19]. For example, vinylcymantrene and vinylferrocene exhibit *e*-values (from the Alfrey—Price *Q*-*e* scheme) of —1.99 and —2.1, respectively, in copolymerizations with styrene. This means the vinyl group, in both the organometallic monomers, is more electron-rich than that of 1,1-di-*p*-anisylethylene (e = —1.96) in vinyl polymerizations.

(η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) is isoelectronic



with vinylcymantrene. Thus, it was of great interest to compare their addition polymerization reactivity. Monomer IV has now been prepared in good overall yield from I according to the sequence outlined in Scheme 1.

η^5-Cyclopentadienyldicarbonylnitrosylchromium (I, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$), was acetylated by the method of Fischer and Plesske [17] to give (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (II) in 50—65% yields. Reduction of II with sodium borohydride in ethanol gave (η^5-1-hydroxyethylcyclopentadienyl)dicarbonylnitrosylchromium (III) in 88% yield. Acid-catalyzed dehydration of III in refluxing benzene, using *p*-tolunenesulfonic acid, in the presence of hydroquinone as a radical inhibitor, gave IV in yields as high as 86%. (η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) is a red liquid, b.p. 79—80°C/0.3 mmHg, which can be purified by repeated vacuum distillation. Such purification is important because alcohol III, as well as the ether formed with ethanol under dehydration conditions when traces of ethanol remain in III, contaminate IV. The IR and PMR spectra of IV agree with this structure and satisfactory analyses were obtained (see Experimental).

(η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) has been homopolymerized and copolymerized with styrene, *N*-vinyl-2-pyrrolidone, and vinylcymantrene (Scheme 2). A series of copolymerizations with styrene has been carried out to determine the reactivity ratios of this unusual monomer. In each copolymerization, the disappearance of monomers was followed quantitatively by GLC as a function of percent conversion. Internal standard techniques and electronic integration were employed. In this way, several composition-conversion data points could be achieved for each individual copolymerization experiment (see Table 1). This method permitted the maximum experimental use of small amounts of monomer IV. The composition-conversion data then were fitted to the integrated form of the copolymer equation by the nonlinear least squares method of Tidwell and Mortimer [20]. Furthermore, after crude values for the reactivity ratios were obtained, further experiments were carried out at

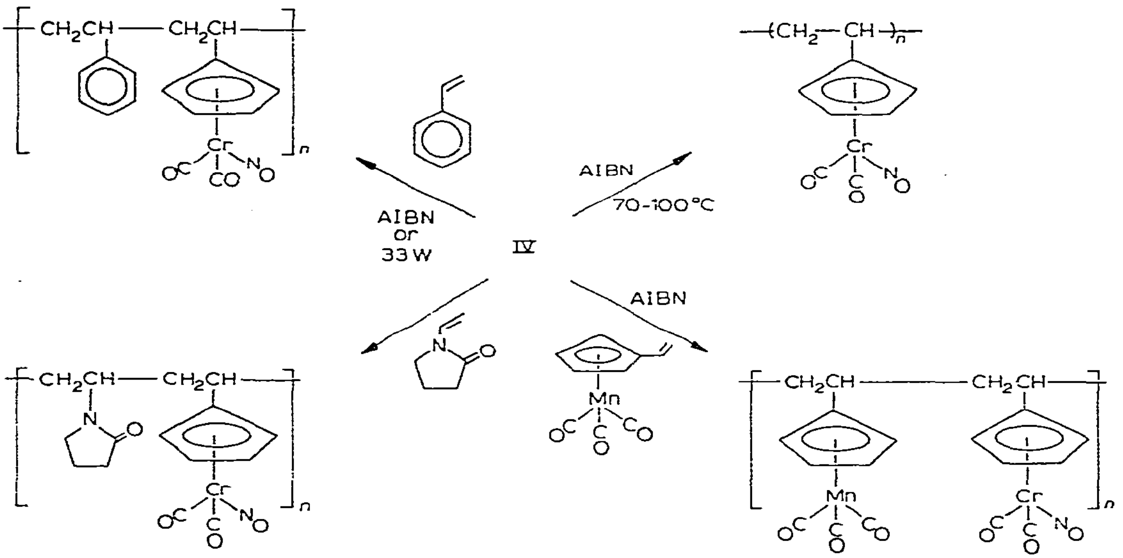


TABLE 1

COMPOSITION-CONVERSION DATA FOR COPOLYMERIZATIONS OF (η^5-VINYLCYCLOPENTADIENYL)DICARBONYLNITROSYLCHROMIUM (IV) WITH STYRENE (M_2)

Run	Monomer IV in feed (mol %)	Conversion (%)	Monomer IV 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 $r_2 = 0.82$.

optimized M_1^0/M_2^0 ratios. The values of r_1 and r_2 were determined as 0.30 and 0.82, respectively (where M_2 is defined as styrene and M_1 as IV).

Since it had been demonstrated that vinylferrocene and vinylcymantrene behave as enormously electron-rich vinyl monomers in radical copolymerizations [19], (the value of *e* in the Price *Q*-*e* scheme [21] for vinylcymantrene in copolymerizations with styrene was $e_1 = -1.99$), the *e*-value was determined for (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) in styrene copolymerizations. Using $r_1 = 0.30$, $r_2 = 0.82$ and $e_2 = -0.80$ (for styrene), a value of $e_1 = -1.98$ is calculated for (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) from the relationship $r_1r_2 = \exp(-(e_1-e_2))$ [2]. Reactivity ratio and *Q*-*e* scheme studies were also performed with other comonomers, such as *N*-vinyl-2-pyrrolidine, with similar results. It is clear the vinyl reactivity of (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) closely resembles that of vinylcymantrene.

In order to appreciate just what this high negative e_1 value means, consider the following values of *e* for selected monomers [22]: maleic anhydride, +2.25; acrylonitrile, +1.20; styrene, −0.80; *p*-*N*,*N*-dimethylaminostyrene, −1.37; and 1,1-di-*p*-anisylethylene, −1.96. Quite obviously, (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) has a very electron-rich double bond. It should undergo cationic, and resist anionic, polymerization. It is therefore established that the vinyl copolymerization behavior of IV is very similar to that of vinylcymantrene. Furthermore, the molecular weight distribution for both bulk and benzene solution homopolymerizations of (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) resembles that found for vinylcymantrene.

Additional copolymerization studies are currently underway involving IV and other monomers to afford polymers with novel and potentially useful properties. In this regard, η^5-cyclopentadienyldicarbonylnitrosylchromium (I) and several of its derivatives have been shown to effectively catalyze various reactions such as hydrogenation [23]. Further, based on recent studies by Alt and Herberhold [24,25], the possibility of preparing novel chiral monomers and polymers derived from I now clearly exists.

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/benzophenone. Merck silica gel was used for column chromatography. *N*-Vinylpyrrolidene and styrene were vacuum distilled from calcium hydride and (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV) 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.

(η^5-1-Hydroxyethylcyclopentadienyl)dicarbonylnitrosylchromium (III). (η^5-Acetylcyclopentadienyl)dicarbonylnitrosylchromium (2.2g) [17] 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, 15 ml of 6 *N* sodium hydroxide was added and the mixture heated on a steam bath for 15 min, the ethanol was removed under vacuum, and the product extracted with ethyl ether. The ether was removed, leaving a red oil; b.p. 105—110°C/0.3 mmHg; 1.95 g (88%). IR (neat): ν(CO) 1945, 2018 cm^{-1}; ν(NO) 1680 cm^{-1}; ν(OH) 3350 cm^{-1}; PMR ($CDCl_3$): τ (ppm) 4.80, m, $H_{2,5}$; 5.05, t, $H_{3,4}$; 5.42, q, methine; 7.55, s, OH; 8.60, d. methyl. Found: C, 44.30; H, 3.73; N, 5.38%. $C_9H_9CrNO_4$ calcd.: C, 43.73; H, 3.67; N, 5.67%.

(η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV). ($^5\eta$-1-Hydroxyethylcyclopentadienyl)dicarbonylnitrosylchromium (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 was 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 liquid, b.p. 79—80°C/0.3 mmHg; 0.41 g (86%). IR (neat): ν(CO) 1952, 2030 cm^{-1}; ν(NO) 1700 cm^{-1}; PMR ($CDCl_3$): τ (ppm) 3.5—4.9, m (ABC), vinyl; 4.85, m, $H_{2,5}$; 5.08, t. $H_{3,4}$. Found: C, 47.41; H, 3.10; Cr, 22.46; N, 6.36%. $C_9H_7CrNO_3$ calcd.: C, 47.17; H, 3.08; Cr, 22.69; N, 6.11%.

Homopolymerization. (η^5-Vinylcyclopentadienyldicarbonylnitrosylchromium (1.072 g, 4.6 mmol), azoisobutyronitrile (0.0024 g, 0.015 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 then was 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 poly(η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium. The IR of the polymer contained carbonyl stretching bands at 2020 and 1930 cm^{-1} and a nitrosyl stretch at 1680 cm^{-1}. In another run, (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (0.5 g) was mixed with azoisobutyronitrile (5 mg), followed by heating to 100°C for 2 h, followed by the addition of another 5 mg of azoisobutyronitrile. After an additional 3 h, methanol (2 ml) was added, the precipitated polymer was washed with excess methanol and dried giving 56 mg (11%) yield of poly(η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium. Gel permeation chromatography of this sample revealed a broad molecular weight distribution with a low $\bar{M}_n$.

Copolymerizations. All copolymerizations were performed in dried, deoxygenated benzene at 70°C in 3 ml mininert® sample vials stirred magnetically In each case, the disappearance of the monomers was followed by GLC. A typical run is described for one (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV)/styrene copolymerization. (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (IV), styrene, naphthalene (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 one hour was allowed after each initiator injection before sampling the reaction for GLC analysis. In some reactions, azoisobutyronitrile 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″ × 50 cm, OV-101 (5%) on Chromosorb 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 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).

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