Kinetics of Radical-Initiated Addition Homopolymerization of η^5-(Vinylcyclopentadienyl)tricarbonylmanganese

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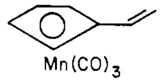
ABSTRACT: The kinetics of the radical-initiated solution homopolymerization of η^5-(vinylcyclopentadienyl)tricarbonylmanganese (hereafter called vinylcymantrene) were studied in benzene, benzonitrile, and acetone. In each solvent the rate was half order in initiator (i.e., AIBN) and three-halves order in monomer. Specifically, the rate equations at 60 °C were $V_p = 1.303 \times 10^{-4}[M]^{1.45}[AIBN]^{0.48}$ in benzene, $V_p = 1.980 \times 10^{-4}[M]^{1.58}[AIBN]^{0.47}$ in benzonitrile, and $V_p = 1.500 \times 10^{-4}[M]^{1.54}[AIBN]^{0.47}$ in acetone. Here V_p is expressed in mol L^{-1} s^{-1} and k in L mol^{-1} s^{-1}. The homopolymerization rates were followed by dilatometry and density data for this monomer are presented. A rate equation of the form $V_p = k[M]^{1.5}[I]^{0.5}$ was derived assuming that the initiator efficiency was low and therefore the initiation process was proportional to [M] (i.e., $f = f'[M]$). If this is correct, then the DP $= V_p/V_i = [k_p/(2f'k_tk_d)^{0.5}][[M]/[I]]^{0.5}$. Molecular weight measurements confirmed that the degree of polymerization was proportional to $([M]/[I])^{0.5}$ in agreement with this treatment. These results are compared to the kinetics of vinylferrocene homopolymerization which were found previously to follow the rate law $V_p = 5.64 \times 10^{-4}[M]^{1.12}[I]^{1.11}$ in benzene and to exhibit a unimolecular termination mechanism.

The novel organometallic monomer, η^5-(vinylcyclopentadienyl)tricarbonylmanganese (**1**), is commonly named vinylcymantrene.[1] Recently, the reactivity ratios for the copolymerization of **1** and a number of common organic monomers were reported, and from these studies the Q and e values were assigned.[2-4] Vinylcymantrene has an exceptionly electron-rich vinyl group as indicated by its large negative e value (approximately -2).[2] This may be compared to the value of e for 1,1-dianisylethylene of -1.96. The homopolymerization of vinylcymantrene has been largely unstudied since it was first reported to occur during the dehydration of η^5-(1-hydroxyethylcyclopentadienyl)tricarbonylmanganese over $KHSO_4$ at 170 °C.[5] Vinylcymantrene is an analogue of vinylferrocene (**2**) and vinylcynichrodene (**3**),[6,7] and these three represent a classic series of organometallic monomers to compare with styrene.



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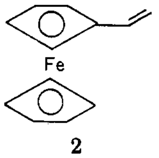

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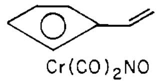

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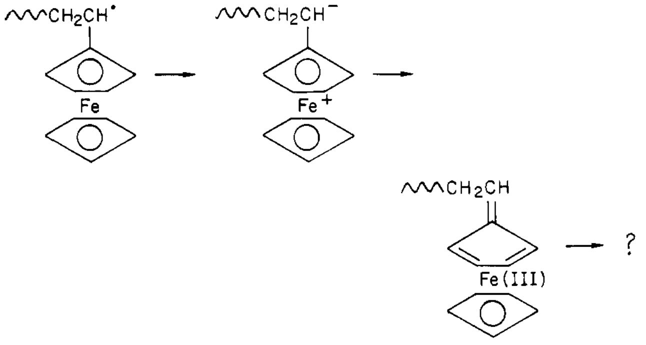
Already the homopolymerization of vinylferrocene (**2**) has proved to be exceptionally interesting. The homopolymerization kinetics of **2**, initiated by AIBN, are first order in *both* monomer and initiator in benzene solutions[8,9] (see eq 1). However, in dioxane solutions the kinetics were

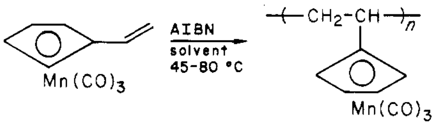
$$V_p = 5.64 \times 10^{-4}[\mathbf{2}]^{1.12}[AIBN]^{1.11} \text{ in benzene} \quad (1)$$

$$V_p = 5.99 \times 10^{-5}[\mathbf{2}]^{0.97}[AIBN]^{0.42} \text{ in dioxane} \quad (2)$$

where V_p = mol L^{-1} s^{-1} and k = L mol^{-1} s^{-1}

found to be first order in monomer and half order in initiator (see eq 2). A monomolecular termination mechanism occurred in benzene which was thought to be caused by electron transfer from iron to the radical center, followed by rearrangement and subsequent decomposition to a paramagnetic Fe(III) species in the polymer.[10,11] This pathway was supported by both ESR and Mössbauer spectroscopy.[9-11] Such Fe(III) species were not present in poly(vinylferrocene) which was prepared in dioxane. Based on this unusual electron-transfer mechanism in poly(vinylferrocene) termination and the close resemblance in copolymerization behavior between monomers **1** and **2**, we decided to investigate the homopolymerization kinetics of vinylcymantrene.





Experimental Section

Materials. Vinylcymantrene was prepared according to previously published accounts.[2-4] The monomer was purified by elution from a silica gel column and vacuum distillation where a center cut was collected (bp 64–65 °C (0.01 mmHg)). After a second identical distillation, the monomer appeared quite pure by GLC, TLC, and high pressure LC analyses.

2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized three times from methanol, dried at ambient temperature, and stored in the dark in sealed tubes under nitrogen at about −15 °C (mp 101–102 °C dec). Benzene and benzonitrile were freshly distilled (from CaH_2); acetone was freshly distilled (from $CaCl_2$).

Homopolymerization Kinetics. Homopolymerization kinetics were followed by measurement of the volume contraction of the solution during polymerization. A dilatometer of the type described by Baldwin[12] was used. Vinylcymantrene, AIBN, and solvent were weighed directly into the sample bulb which was then attached to the remainder of the dilatometer by means of metal springs and a ground glass joint. A mercury reservoir was located below the sample bulb at the end of a narrow bore tube having an internal diameter of 0.989 mm at 60 °C. The system was then degassed by five freeze–pump–thaw cycles at about 10^{-3} to 10^{-4} mmHg. After the fifth evacuation, the dilatometer was inverted so that mercury filled the bore and bottom of the sample bulb. The reservoir was removed and the dilatometer placed in a constant temperature (±0.01 °C) water bath at the desired temperature. After temperature equilibrium was reached (about 4 min) the volume contraction was followed by measuring the rate at which the mercury column dropped. The number of moles of

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monomer which had polymerized was obtained by dividing the value of ΔV_{ob} by the molar volume contraction constant, $\Delta V/\text{mol}$.

The specific volume changes that occurred during polymerizations in benzonitrile were determined using a 25 mL pycnometer with a long narrow bore neck. The neck bore volume and diameter were determined at 50, 60, and 70 °C using known weights of distilled water. A cathometer was used to measure the meniscus' distance from the calibration mark. Using the calibrated pycnometer, the specific volumes of benzonitrile, vinylcymatrene (11.2 wt % in benzonitrile solution), and poly(vinylcymantrene) (2.1 wt % in benzonitrile) were determined at 50, 60, and 70 °C. From these data, the changes in specific volume which occur during polymerization at 50, 60, and 70 °C were determined to be −20.21, −20.42, and −21.23 mL mol^{-1}, respectively. For the studies in benzene and acetone, the density of vinylcymantrene was determined by standard pycnometer measurements. The apparent density of poly(vinylcymantrene) was obtained by standard dilatometer measurements.[13]

Isolation and Characterization. After removing the dilatometer from the bath, the polymer was precipitated into ~700 cm^3 of rapidly stirred petroleum ether (30–60 °C) at room temperature. Care was taken to insure the formation of very fine particles of polymers. The polymer was redissolved and precipitated three more times to be certain that all monomer had been removed. The precipitate was filtered, dried at ~1 mmHg, and weighed. Infrared spectra (KBr) of poly(vinylcymantrene) were completely devoid of the C═C stretching band at 1636 cm^{-1} present in the monomer. Key absorptions were found at 3098, 2990–2865, 2010 (vs), 1921 (vs), 1480, 1390, 1290, 1262, 1031, 899, 827, 656, and 624 cm^{-1}. The spectra were essentially identical to previously isolated samples which had been thoroughly analyzed.[2-4]

A Waters Associates Model 200 gel permeation chromatograph, equipped with a 16 ft. styragel column bank, was used for GPC measurements. The polymers were chromatographed in THF and the chromatograms analyzed using the Universal calibration method[14] employing a polystyrene standard calibration curve. The intrinsic viscosities of poly(vinylcymantrene), used for this calibration, were measured in THF at 30 ± 0.02 °C using a Cannon-Ubbelohde semimicro dilution viscometer. The sedimentation equilibrium measurements were perfomed at low speed (5×10^3 to 20×10^3 rpm in benzene) using a Beckman, Model E, analytical ultracentrifuge with ultraviolet absorption optics and a photoelectric scanner. The membrane osmometry determinations were performed commercially in THF.

Results

Synthesis and Density Measurements. Vinylcymantrene (1) was prepared, as previously described,[4,15] by the $AlCl_3$-catalyzed acylation of cymantrene followed by sodium borohydride reduction and dehydration over $KHSO_4$ at 190 °C in the presence of hydroquinone. The monomer was purified to TLC purity by column chromatography (silica gel) and vacuum distillation. The homopolymerization kinetics were studied by dilatometric techniques[12] in benzene, benzonitrile, and acetone. Benzene was chosen in order to compare the homopolymerizations of vinylcymantrene with those of vinylferrocene. The more polar solvents, acetone and benzonitrile, were good solvents for poly(vinylcymantrene). Azobis(isobutyronitrile) was selected because it had been the initiator used in previous copolymerization studies of vinylcymantrene[2-4] and in the vinylferrocene homopolymerizations.[8-11]

In dilatometric determinations, calculation of the volume contraction from the densities of the pure monomer and polymer is only valid for bulk polymerizations. The errors introduced by using bulk densities have been discussed by Treloar[16] and Morris and Parts.[17] For accurate measurements, the apparent density of the monomer and polymer should be determined in the polymerization solvent at the reaction temperature used and in a concentration close to that employed in the polymerization.[13] Thus, the density and apparent density of vinylcymantrene were obtained in benzonitrile, benzene, and acetone (Table I). Plots of these densities as a function of temperature, shown in Figure 1, demonstrate the densities have a linear dependence on temperature. The bulk of the kinetic measurements were performed at 60 °C where the apparent densities of poly(vinylcymantrene), employed to calculate percent conversion, were: 1.539 g cm^{-3} in benzene, 1.506 g cm^{-3} in benzonitrile, and 1.531 g cm^{-3} in acetone.

Rates of Polymerization. The kinetic runs were performed at 60 ± 0.1 °C. The effects on rate of varying

Table I
Density of Vinylcymantrene (1) and Apparent Densities of Vinylcymantrene in Benzene and Acetone

temp, °C	density of 1, g cm^{-3}	apparent density of 1, g cm^{-3} in benzene[a]	apparent density of 1, g cm^{-3} in acetone[b]
30.0			1.393
35.0	1.361	1.371	
37.0			1.386
40.0	1.355	1.367	
45.0	1.350	1.364	1.377
50.0	1.343	1.361	1.371
55.0	1.338	1.358	1.365
60.0	1.332	1.354	1.358
65.0	1.326		
65.1		1.350	
70.0	1.321	1.347	
75.0	1.315	1.344	
80.0	1.309		

[a] As a 44.11 wt % solution in benzene. [b] As a 44.23 wt % solution in acetone.

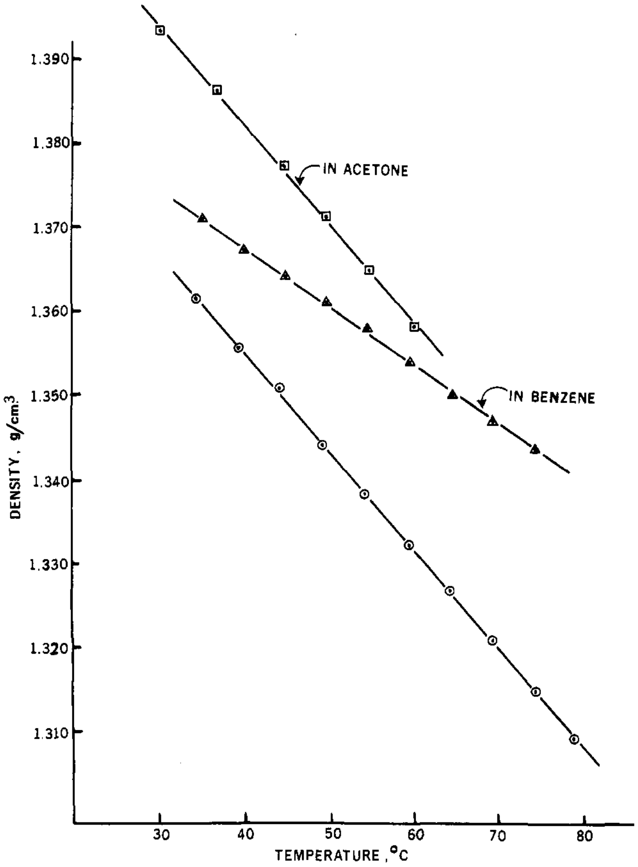

Figure 1. Plot of the density of vinylcymantrene vs. temperature and plots of its apparent density in benzene and acetone vs. temperature: ⊙, density neat; △, density in benzene; and ⊡, density in acetone.

Table II
Homopolymerization of Vinylcymantrene in Benzene, Acetone, and Benzonitrile Solutions, Initiated by AIBN at 60 °C (Monomer Concentration Constant)

polymer no.[a]	[M], mol L^{-1}	[I] × 10^2, mol L^{-1}	conversion, %	V_p × 10^5, mol L^{-1} s^{-1}
B1	2.00	1.00	7.1	3.88
B2	2.00	2.00	7.2	5.34
B3	2.00	3.00	7.1	6.63
B4	2.00	4.00	5.6	7.49
B5	2.00	5.00	6.4	8.36
A2	2.00	1.00	6.7	5.20
A4	2.00	2.00	7.1	7.04
A3	2.00	3.00	7.3	8.58
A5	2.00	4.00	7.5	9.75
A1	2.00	5.00	7.6	10.70
BN1	0.748	2.460	10.6	2.41
BN2	0.748	5.669	12.1	3.29
BN3	0.729	0.960	7.7	1.43
BN4	0.752	3.423	5.0	2.76
BN5	0.746	1.743	8.3	2.07

[a] B represents polymerizations in benzene, A in acetone, and BN in benzonitrile.

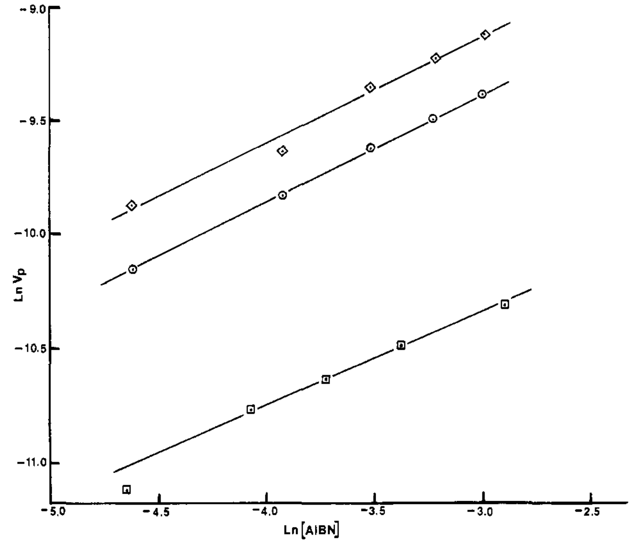

Figure 2. Plots of ln V_p vs. [AIBN] for vinylcymantrene homopolymerizations in benzene, acetone, and benzonitrile at 60 °C. The [M] is held constant: ⊙, in benzene; ◇, in acetone; and ⊡, in benzonitrile.

the initiator concentration, [AIBN], while holding the vinylcymantrene concentration constant, are tabulated in Table II for the solvents benzene, benzonitrile, and acetone, respectively. Plots of ln V_p vs. ln [AIBN] are shown in Figure 2 for benzene, acetone, and benzonitrile. The plots are linear and the slopes (determined by least-squares analysis) were 0.48 in benzene, 0.47 in benzonitrile, and 0.47 in acetone. Clearly, in each solvent the polymerization rate is half order in initiator and a bimolecular termination process is operating unlike the monomolecular termination found in vinylferrocene homopolymerizations.

The effects on V_p of varying the monomer concentration, [M], at constant initiator concentration, are tabulated in Table III for benzene, benzonitrile, and acetone. The corresponding plots of ln V_p vs. ln [M] are shown in Figures 3 and 4. Again the plots are linear with high correlation coefficients. The slopes were 1.45 in benzene, 1.58 in benzonitrile, and 1.54 in acetone. Therefore, in all three solvents *the rate is three-halves order in vinylcymantrene.*

The values of the rate constant, *k*, are recorded in Table IV for each solvent. The rate constants are, indeed, reasonably constant and their average values are 1.303 × 10^{-4} in benzene, 1.980 × 10^{-4} in benzonitrile, and 1.500 × 10^{-4} in acetone when V_p is expressed in mol L^{-1} s^{-1} and *k* in L mol^{-1} s^{-1}. Thus, at 60 °C the rate expressions for vinylcymantrene homopolymerizations are:

Table III
Homopolymerization of Vinylcymantrene in Benzene, Acetone, and Benzonitrile Solutions Initiated by AIBN at 60 °C (Initiator Concentration is Constant)

polymer no.[a]	[M], mol L^{-1}	[I] × 10^2, mol L^{-1}	conversion, %	V_p × 10^5, mol L^{-1} s^{-1}
B7	1.00	2.00	6.3	2.01
B6	1.50	2.00	7.2	3.53
B8	1.75	2.00	7.2	4.73
B2	2.00	2.00	7.2	5.34
A6	1.00	2.00	8.1	2.36
A7	1.50	2.00	7.7	4.22
A8	1.75	2.00	7.5	5.67
A4	2.00	2.00	7.1	7.04
A9	2.50	2.00	7.5	9.46
BN6	0.102	2.49	4.6	0.077
BN7	0.248	2.49	6.0	0.434
BN8	0.490	2.43	10.5	1.250
BN9	1.005	2.49	10.1	3.63
BN10	1.567	2.52	15.5	6.56
BN11	1.997	2.45	15.2	8.88

[a] B represents polymerizations in benzene, A in acetone, and BN in benzonitrile.

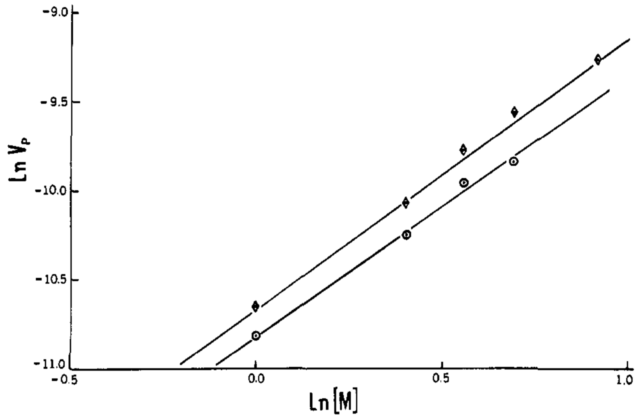

Figure 3. Plots of ln V_p vs. [M] for vinylcymantrene homopolymerizations in benzene and acetone at 60 °C. The [I] is held constant: ⊙, in benzene; and ◇, in acetone.

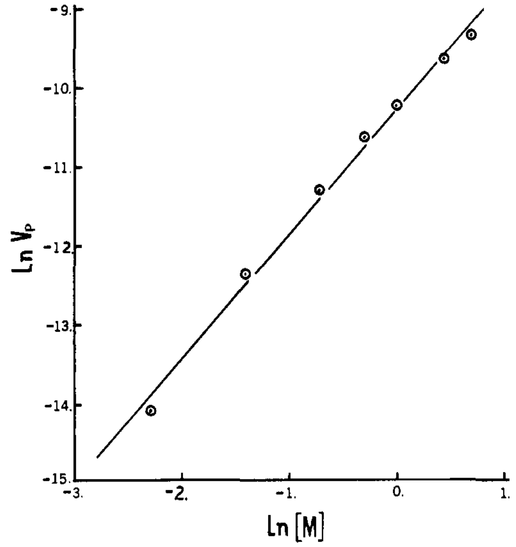

Figure 4. Plot of ln V_p vs. [M] for vinylcymantrene homopolymerizations in benzonitrile at 60 °C. The [I] is held constant.

$$V_p = 1.303 \times 10^{-4}[1]^{1.45}[\mathrm{AIBN}]^{0.48} \text{ in benzene} \quad (3)$$

$$V_p = 1.980 \times 10^{-4}[1]^{1.58}[\text{AIBN}]^{0.47} \text{ in benzonitrile} \quad (4)$$

$$V_p = 1.500 \times 10^{-4}[1]^{1.54}[\text{AIBN}]^{0.47} \text{ in acetone} \quad (5)$$

Next, studies were made to determine the activation energy. The effect of temperature on V_p, at constant monomer and initiator concentrations, is shown in Table V for each of the three solvents. Arrhenius plots of these data are shown in Figure 5 for benzene, acetone, and benzonitrile. The overall values of activation energy, E_0, were found to be 22.2 kcal mol^{-1} in benzene, 21.0 kcal mol^{-1} in benzonitrile, and 22.3 kcal mol^{-1} in acetone.

Molecular Weights. Several representative molecular weight measurements were performed on poly(vinylcymantrene) homopolymers (see Table VI). These molecular weights were determined by gel permeation chromatography using the Universal calibration method.[14] Studies in this laboratory[18] and others[19] have shown the weight averaged molecular weights obtained by GPC are reasonably accurate, but the number averaged molecular weights are frequently too low leading to errors in values of $\overline{M}_w/\overline{M}_n$. Thus, equilibrium sedimentation and membrane osmometry experiments were used to determine $\overline{M}_n$ values. It is clear that high polymers are obtained and the usual kinetic analyses can be applied.[20]

Discussion

Kinetic Scheme. The usual kinetic analysis of addition polymerization considers initiation, propagation, and termination. Thus:

$$V_i = 2k_d f[\text{I}] \quad (6)$$

$$V_p = -\text{d}[\text{M}]/\text{d}t = k_p[\text{M}][\text{R}\cdot] \quad (7)$$

$$V_t = k_t[\text{R}\cdot]^2 \quad (8)$$

where V_i, V_p, and V_t are the rates of initiation, propagation, and termination, respectively, and k_d, k_p, k_t, and f have the usual meanings. Applying the steady-state approximation, $V_i = V_t$, solving for [R·], and substituting this expression into the equation for the propagation rate leads to:

$$V_p = -\text{d}[\text{M}]/\text{d}t = k_p\left(\frac{2fk_d[\text{I}]}{k_t}\right)^{0.5}[\text{M}] \quad (9)$$

or

$$V_p = k_{\text{obsd}}[\text{M}][\text{I}]^{0.5} \quad (10)$$

In contrast to eq 10, we found that the rate of polymerization, V_p, was not proportional to the first power of monomer concentration. Instead, the rate depended on [vinylcymantrene]$^{3/2}$ in all three solvents studied (i.e., benzene, benzonitrile, and acetone). In the analysis above, f is independent of [M] and the rate is proportional to the first power of monomer concentration. This holds true if the initiator efficiency is high. If the initiator efficiency was very low, f may become proportional to [M] according to:

$$f = f'[\text{M}] \quad (11)$$

Substituting this expression for f into eq 9 gives:

$$V_p = k_p\left(\frac{2f'k_d[\text{I}][\text{M}]}{k_t}\right)^{0.5}[\text{M}]^1 \quad (12)$$

or

$$V_p = k_{\text{obsd}}[\text{I}]^{0.5}[\text{M}]^{1.5} \quad (13)$$

The rate expression (13) would also apply if the initiator was being decomposed by the monomer at a significantly faster rate than it decomposes thermally. To test this possibility, two equal volumes of AIBN (1 M in benzene) were thermally decomposed at 70 °C. One solution contained vinylcymantrene (1 M) while the other solution did not. Measurement of nitrogen evolution showed the rates of decomposition were equal. Thus, the vinylcymantrene-induced decomposition of AIBN is not a factor in the observed kinetics.

Table IV
Values of the Rate Constant for Vinylcymantrene Homopolymerization at 60 °C Initiated by AIBN in Benzene, Acetone, and Benzonitrile

polymn no.	k^a	polymn no.	k^b	polymn no.	k^c
B1	1.30	A1	1.50	BN1	2.17
B2	1.28	A2	1.56	BN2	2.00
B3	1.31	A3	1.53	BN3	2.09
B4	1.29	A4	1.52	BN4	2.11
B5	1.29	A5	1.52	BN5	2.20
B6	1.28	A6	1.48	BN6	1.61
B7	1.31	A7	1.42	BN7	2.23
B8	1.36	A8	1.51	BN8	2.22
		A9	1.45	BN9	2.04
				BN10	1.82
				BN11	1.70

[a] $k = V_p \times 10^4/[\text{M}]^{1.45}[\text{I}]^{0.48}$. [b] $k = V_p \times 10^4/[\text{M}]^{1.54} \times [\text{I}]^{0.47}$. [c] $k = V_p \times 10^4/[\text{M}]^{1.58}[\text{I}]^{0.47}$.

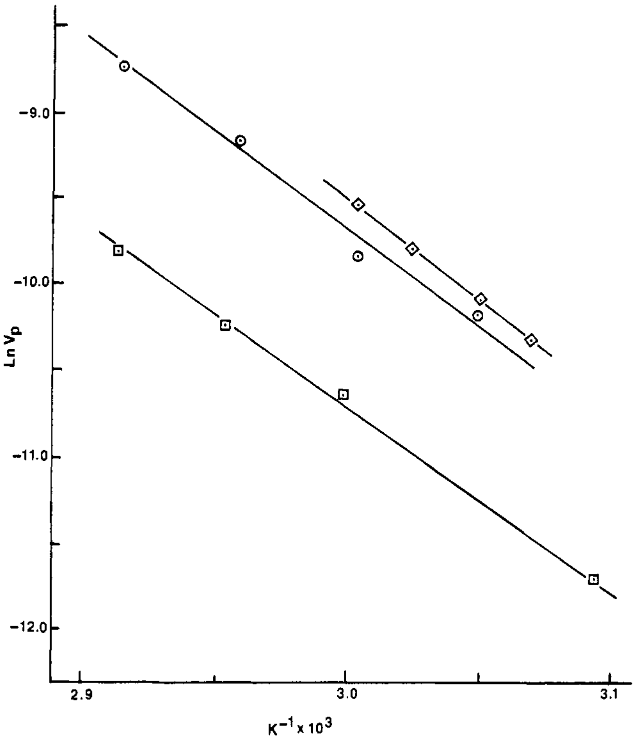

Figure 5. Plots of ln V_p vs. the reciprocal of absolute temperature for vinylcymantrene homopolymerizations in benzene, acetone, and benzonitrile: ⊙, in benzene; ◇, in acetone; and ⊡, in benzonitrile.

Activation Energy for Propagation. The overall activation energies E_0 for vinylcymantrene homopolymerizations were 22.2, 21.0, and 22.3 kcal mol^{-1} in benzene, benzonitrile, and acetone, respectively. The rate constants for polymerization, initiation, propagation, and termination are related to their respective activation energies and are expressed in Arrhenius form according to:

$$E_0 = E_p + 0.5(E_d - E_t) \quad (14)$$

where E_p, E_d, and E_t are the activation energies for

Table V
Dependence of Vinylcymantrene Homopolymerization Rate on Temperature in Benzene and Acetone Solution

polymn no.[a]	[M], mol L^{-1}	[I] × 10^2, mol L^{-1}	temp, °C	conversion, %	$V_p \times 10^5$, mol L^{-1} s^{-1}
B11	2.00	2.00	55.0	6.9	3.81
B2	2.00	2.00	60.0	7.2	5.34
B9	2.00	2.00	65.0	6.9	10.31
B10	2.00	2.00	70.0	7.5	15.94
A12	2.00	2.00	52.5	7.7	3.30
A11	2.00	2.00	55.0	7.5	4.03
A10	2.00	2.00	57.5	7.4	5.52
A4	2.00	2.00	60.0	7.1	7.04
BN12	0.750	2.50	50.0	7.3	0.81
BN1	0.748	2.46	60.2	10.6	2.41
BN13	0.746	2.48	65.4	6.8	3.57
BN14	0.754	2.47	70.1	9.1	5.49

[a] B represents polymerizations in benzene, A in acetone, and BN in benzonitrile.

propagation, initiator decomposition, and termination, respectively. The literature[21] value for E_d of AIBN is 30.34 kcal mol^{-1} in benzene at 60 °C, and it does not vary appreciably with changes in solvent. The activation energy for termination in vinylcymantrene polymerizations is not known but $E_t \simeq$ 1.9 kcal mol for polystyrene. For this discussion 1.9 may be used as an approximation for E_t for poly(vinylcymantrene). Previously, George and Hayes[9] made this same approximation in their treatment of the kinetics of vinylferrocene homopolymerizations. Substitution of the values of E_0, E_d, and E_t into eq 14 gives the following values of E_p for the propagation reaction of vinylcymantrene: 8.0 kcal mol^{-1} in benzene, 6.8 kcal mol^{-1} in benzonitrile, and 8.1 kcal mol^{-1} in acetone.

The values of E_p for vinylcymantrene homopolymerization, obtained above, are all close to that of polystyrene (6.3 kcal mol) and within the 3.5 to 10 kcal mol range expected for rapid radical addition reactions.[22] These values of E_p are slightly higher than those obtained for vinylferrocene homopolymerizations. In benzene,[9] where vinylferrocene gave monomolecular termination, its value of E_p = 4.78 kcal mol^{-1} and in dioxane[23] E_p = 5.86 kcal mol^{-1}.

Degree of Polymerization. In previous studies of vinylferrocene homopolymerizations, two groups[8,24] found that the molecular weight did not increase when the [M]:[I] ratio was increased in benzene. This resulted because the termination step was monomolecular which required the following equation for the degree of polymerization.

$$\overline{DP} = k_p[M]/k_t \qquad (15)$$

Thus, $\overline{DP}$ was independent of [I] at constant temperature. The situation for vinylcymantrene, however, is different. The kinetic chain length is defined as the number of monomer units consumed per active center.[25] It is therefore given by V_p/V_i. For vinylcymantrene we concluded that the initiation expression was:

$$V_i = 2f'k_d[I][M] \qquad (16)$$

Also, V_p was given in eq 12. Dividing (12) by (16) one obtains eq 17 which relates the $\overline{DP}$ of vinylcymantrene to the monomer and initiator concentrations.[25]

$$\overline{DP} = \frac{k_p}{(2f'k_tk_d)^{0.5}}\left(\frac{[M]}{[I]}\right)^{0.5} \qquad (17)$$

Since the polymer samples studied in this paper were all isolated from reactions to low conversions, the use of $[M]_0$ and $[I]_0$ (i.e., initial concentrations) appears justified. Equation 17 predicts the molecular weight of poly(vinylcymantrene) should be proportional to $([M]/[I])^{1/2}$. This relationship appears to hold. For example, as the $[M]_0/[I]_0$ ratio was varied from 250 to 40 in benzene solution homopolymerizations at 60 °C, the values of $\bar{M}_n$ decreased from 42.4 × 10^3 to 17.5 × 10^3 (see Table VI). For a series of polymerizations, in both benzene and acetone, the value of $\bar{M}_n/([M]/[I]^{0.5}$ remained approximately constant (see Table VI) as predicted by eq 17.

Both the kinetics (eq 12 and 13) and the degree of polymerization data (eq 17 and Table VI) support a polymerization mechanism where the initiator efficiency is very low and $f = f'[M]$ in vinylcymantrene homopolymerizations. It should be noted that other workers have observed monomer orders greater than one. For example, DeSchrijver and Smets[26] found that the addition of polystyrene to styrene homopolymerizations caused the order in monomer to increase above one and the order in initiator to decrease below one-half. This was due to an increase in solution viscosity which occurred when polystyrene was added. The order in monomer increased due to a decrease in initiator efficiency while the initiator order decreased due to a decrease in the rate of bimolecular chain termination. However, in the vinylcymantrene homopolymerizations described above, no great change in viscosity occurred during the polymerizations. All reactions were run to low conversion (5–8%). Also, the orders in initiator remained one-half. Thus, an inherently low initiator efficiency best explains our results and complications from viscosity changes may be neglected.

The gel permeation chromatograms of the vinylcymantrene homopolymers gave smooth single peak curves. The molecular weight distributions appeared to be broad. These chromatograms did not exhibit the binodal peaks which have often been found in poly(vinylferrocene) samples.[10,11,24]

Table VI
Molecular Weights for Representative Homopolymers of Vinylcymantrene Prepared in Benzene and Acetone

polymn no.	[M]/[I]	conversion, %	$\bar{M}_n \times 10^{-3}$ from GPC[a]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$ from GPC[a]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n/([M]/[I])^{0.5} \times 10^{-3}$
B12	250	6.4	22.7	42.4[c]	361.0	8.5	2.68
B1	200	7.1	16.3	39.1[c]	334.0	8.9	2.77
B2	100	7.2	8.6	26.4[b]	162.0	6.1	2.64
B7	75	6.3	7.9	23.3[b]	82.1	3.5	2.70
B5	40	6.4	7.3	17.5[b]	51.3	2.9	2.81
A13	250	6.8	16.6	49.2[c]	162.0	3.3	3.11
A2	200	6.7	15.3	42.2[c]	135.0	3.2	2.99
A4	100	7.1	11.5	32.5[c]	109.0	3.4	3.25
A7	75	5.9	13.4	25.2[b]	99.6	3.9	2.90
A1	40	7.6	12.1	20.9[b]	91.7	4.4	3.31

[a] Calculated from gel permeation chromatograms run in THF at ambient temperature. [b] Determined by the equilibrium sedimentation method. [c] Determined by membrane osmometry.

This work when coupled with the studies of vinylferrocene (**2**)[9-12,24] and vinylcynichrodene (**3**)[6,7] provides the first detailed examples of the homopolymerization behavior of vinyl organometallic monomers. Interest in such monomers is growing rapidly.[27]

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Polymerization via Zwitterion. 18. Alternating Cooligomerizations of Ethylenesulfonamide with Cyclic Phosphorus Compounds

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ABSTRACT: Alternating cooligomerization of ethylenesulfonamide (ESAm) with cyclic phosphorus compounds, i.e., 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite, EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite, EPI), took place without any added initiator to produce 1:1 alternating cooligomers from ESAm–EPO and ESAm–EPI. The structures of the cooligomers were established by IR and NMR spectra, elemental analyses, as well as the alkaline hydrolysis experiments. The reaction scheme of the cooligomerization via zwitterion (eq 4–6) was proposed.

A series of the new alternating copolymerizations between nucleophilic monomers (M_N) and electrophilic monomers (M_E) via zwitterion intermediates has been found by us.[1] All of these copolymerizations are characterized by the fact that they take place without added catalyst. Recently we have reported the cooligomerization of ethylenesulfonamide (ESAm) with a cooligomer of an amide–sulfonamide structure.[2] In this case ESAm provided a very stable anionic part of a zwitterion derived from a combination of ESAm and 2-methyl-2-oxazoline (M_N), and hence, the key intermediate of genetic zwitterion could even be isolated.[2] In the present study we have adopted two cyclic phosphorus compounds as M_N monomers. They are 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite, EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite, EPI).

Results and Discussion

Cooligomerization and Characterization of Cooligomers. An equimolar mixture of EPO and ESAm (5 mmol each) in benzonitrile (1.5 mL) containing 0.02 mmol of *N*-phenyl-2-naphthylamine as a radical inhibitor was heated at 100 °C under nitrogen. After 42 h the reaction mixture was poured into a large amount of diethyl ether to precipitate the oligomeric product. The cooligomer was dried in vacuo to give 1.06 g of glassy, white, and hygroscopic solids (77% yield).

The structure of the cooligomer was examined by IR and NMR spectroscopy, elemental analysis, and the alkaline hydrolysis experiment of the cooligomer. The IR spectrum