added very slowly to keep the ethylene absorption at an arbitrarily chosen figure of 650 ml. per minute, running water maintaining the reaction at about 20°. Polymerization was continued in this fashion for 4 hours, at which time the rate began to fall off because of stirring difficulties; a total of 8 ml. of diethylaluminum chloride was added. The usual isolation yielded 150 g. of polymer, R.S.V. 3.0.

Polymerization of Ethylene with Bis-(cyclopentadienyl)-titanium Dichloride.—In the reaction flask were placed 500 ml. of dry toluene and 625 mg. (2.5 millimoles) of bis-(cyclopentadienyl)-titanium dichloride. The solution was deaerated as described above, Gulf ethylene containing 0.003 mole % oxygen was passed in, and a 0.96 *M* solution of diethylaluminum chloride in *n*-heptane was added drop by drop. The temperature was maintained at 13° by running water. Polymerization started after 30 minutes, at which time 3.2 ml. (3.0 millimoles) of diethylaluminum chloride had been added; the solution was a greenish-brown. Addition of the aluminum compound was continued and ethylene was absorbed smoothly at 500–650 ml. per minute at 18–19°. The polymerization was continued for 90 minutes, at which time the reaction was stopped with ethanol, and the polymer isolated; 62.5 g. of polymer was obtained, R. S. V. 1 5.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

Kinetics of Ethylene Polymerization Catalyzed by Bis-(cyclopentadienyl)-titanium Dichloride–Dimethylaluminum Chloride[1]

BY JAMES C. W. CHIEN

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The kinetics of ethylene polymerization catalyzed by bis-(cyclopentadienyl)-titanium dichloride–dimethylaluminum chloride has been studied. Initiation was followed by using C^{14}-labeled $(CH_3)_2AlCl$. Instantaneous concentration of propagating metal alkyl complex, [C], was obtained by quenching aliquots of polymerizing mixtures with I_2^{131}. The propagation step was first order in monomer and [C], with an activation energy of 12.2 kcal. mole^{-1}; k_p at 30° was 13.6 ± 1.4 liter mole^{-1} sec.$^{-1}$ Termination was second order with respect to [C] with an activation energy of 16.4 kcal. mole^{-1}; k_t at 30°, and an Al to Ti ratio of 2.5 was 9.07 ± 0.58 liter mole^{-1} sec.$^{-1}$, which decreased with increase of the ratio. Each polymer molecule was found to contain 1.07 ± 0.27 $C^{14}H_3$ groups, thus eliminating a number of transfer processes. These kinetic data were used to calculate number-average molecular weight, $\bar{M}_n$, which agreed well with the ones obtained by fractionation of polymers.

Introduction

The discovery of polymerization of ethylene at low pressure by Ziegler[2] using catalysts which cannot be considered to operate by any of the known polymerization mechanisms has stimulated much investigation. The most studied catalyst systems, usually consisting of a transition metal halide and a metal organic compound, are heterogeneous. Determinations of kinetic parameters in these systems are necessarily difficult. Recently, Breslow and Newburg[3] and Natta and co-workers[4] described a soluble catalyst system consisting of bis-(cyclopentadienyl)-titanium dichloride–alkylaluminum compounds. This catalyst is soluble in toluene, and remains in solution during and after reduction of titanium.

Preliminary studies with such a soluble catalyst in this Laboratory have shown that (1) the life times of growing polymer chains are of the order of tens of minutes, making possible a measurement of their concentrations as a function of time, and (2) alkyl groups of the metal complex catalysts are incorporated in the polymer, enabling a determination of initiation events using C^{14}-labeled metal alkyls. Thus, it is possible to obtain the individual rate constants of the polymerization under nonsteady state conditions. The objective of this investigation was the study of the kinetics of ethylene polymerization by the catalyst $(C_5H_5)_2TiCl_2–(CH_3)_2AlCl$, in order to aid in interpreting the mode of operation of such a catalyst.

Experimental

Materials.—Bis-(cyclopentadienyl)-titanium dichloride was prepared according to the procedure of Wilkinson and Birmingham.[5] Dimethylaluminum chloride labeled with C^{14} was prepared from $C^{14}H_3Cl$ (Tracerlab, Houston, Texas) in a vacuum system according to the method of Grosse and Mavity.[6] Mallinckrodt analytical reagent grade toluene was purified by shaking with concentrated sulfuric acid. This was followed by separation, neutralization, washing, drying over anhydrous magnesium sulfate and filtration. The treated toluene was passed through a 20-in. silica gel column directly into the reaction vessel under an atmosphere of nitrogen. Phillips Petroleum research grade ethylene was used without further purification. It was 99.96% pure, with ethane the major impurity.

Polymerization was carried out in a one-liter reaction vessel equipped with magnetic stirrer, immersed in a constant temperature bath (±0.2°). The monomer pressure was kept constant to ±0.5 cm. at 100 cm. by means of a Hoke low-pressure regulator no. 804. At higher pressures, 175 and 255 cm., constant pressure of ±2 cm. was maintained by a Matheson regulator no. 501. The pressure of the system was measured by calibrated Stratham transducers and recorded. Three calibrated Fisher–Porter triflat flowmeters in parallel arrangement determined the instantaneous rate of monomer consumption. The maximum rates of polymerization were usually 0.02 to 0.05 g. liter^{-1} sec.$^{-1}$. A copper–constantan thermocouple was inserted to measure the internal temperature of the polymerizing mixture. A temperature rise of less than 2° was observed at the peak of a fast polymerization.

Aliquots of fine polymer slurry were taken from the polymerization mixture during a run. This was done with a syringe connected through a Hoke valve (stainless steel throughout with Teflon packings) to a 13-gage 12-in. long hypodermic needle. The sampling technique was found to have a reproducibility of better than 2.0%; 15 to 20 such samples were usually taken at predetermined intervals.

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[1] Presented in part at the Gorden Research Conference on Polymers, New London, N. H., June 30, 1958.

[2] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew Chem.*, **67**, 541 (1955).

[3] D. S. Breslow and N. R. Newburg, THIS JOURNAL, **79**, 5072 (1957).

[4] G. Natta, P. Pino, G. Mazzanti, V. Giannini, E. Mantica and M. Peraldo, *Chim. e ind.* (*Milan*), **39**, 19 (1957); *C.A.*, **51**, 7049 (1957); G. Natta, P. Pino, G. Mazzanti and V. Giannini, THIS JOURNAL, **79**, 2975 (1957).

[5] G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954).

[6] A. V. Grosse and J. N. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

The samples were injected into a heptane solution of iodine containing I_2^{131} of known specific activity. This mixture, kept under nitrogen atmosphere, was allowed to stand at room temperature for a minimum of 2 hours. The excess iodine was then removed by addition of an isopropyl alcohol solution of NaI and an aqueous solution of thiosulfate. The polymer was filtered, washed with heptane repeatedly, boiled for 10 min. with a 10% HCl solution in methanol, followed by washing with methanol until neutral to litmus. The polymer was dried overnight in a vacuum oven at 80°. This method of polymer work-up was shown to give reproducible specific activity to within 2%.

Radioactive Determinations.[7]—The polymer was weighed and packed in a 4.5-sq. cm. copper planchet. The radioactivity was measured by a G.M. end window tube. The total counts were always in excess of 10,000. A correction[8] to infinite thickness was used for I^{131}.

Conversion of I^{131} counting rates to the number of I^{131} atoms in the polymer was achieved by direct comparison with an iodine solution of known concentration (as NaI^{131}) in isopropyl alcohol. No correction for the difference in counting media was needed because the relative attenuation per unit mass of O and C for betas of I^{131} is almost identical.[9] The C^{14}-activity of polymer samples was related to methyl group content by similar comparisons with a stock solution of $(C^{14}H_3)_2AlCl$, aliquots of which were first hydrolyzed and then converted to $BaCO_3$ by standard technique.[10] Cross calibration was done by converting samples of polyethylene containing known counting rates of C^{14} into $BaCO_3$.

Determination of Number-average Molecular Weight.[11]—Number-average molecular weight, $\bar{M}_n$, of polymer samples was determined by fractionation. The molecular weights of the polymer fractions were determined by intrinsic viscosity measurements using relationships calibrated by light scattering data. The fractionation procedure and calculations of $\bar{M}_n$ using both the summative method and Wesslau's distribution function has been described in detail by Francis, Cooke and Elliott.[12] A total of 25 fractionations were performed on samples with $\bar{M}_n$ from 6,100 to 95,300. The average deviation of $\bar{M}_n$'s calculated by these two methods from the mean values was 10.5%. The recovery of polymer from the fractionation column averaged 99.2%, with a standard deviation of 2.25%.

Infrared Determinations of Polymer Unsaturation.[13]—Vinyl ($-CH=CH_2$), vinylidene ($>C=CH_2$) and *trans*-vinylene ($-CH=CH-$) were determined with a Perkin-Elmer model 21 double-beam spectrophotometer, employing the absorption maxima at 11.00, 11.26 and 10.34 μ, respectively. The limit of detection was 0.005% by weight in each case.

Solubility of Ethylene in Toluene.—The solubility of ethylene in toluene was determined by volume–pressure measurements at 0, 15, 30, 45 and 60° and 76, 110, 155 and 200 cm. pressure. Linear dependence of solubility on pressure was obtained at all temperatures. The solubility at 0° and 76 cm. was 0.0775 mole liter^{-1} (Bunsen absorption coefficient at 0° = 1.73). The heat of solution was found to be 2.14 kcal. mole^{-1}.

Results

Chain Initiation.—Initiation is defined here as the formation of an active methyl–metal bond, on which growth subsequently takes place. However, it is not possible to measure this process directly. Instead, initiation was followed by using $(C^{14}H_3)_2AlCl$, and measuring the increment of C^{14} in high polymers with time. Thus, those initiated species, which were terminated while the degree of polymerization was still very low, were not included. The same limitation was applied to the measurements made on both the I^{131} activities and polymer yields.

The C^{14}-results are plotted according to first-order kinetics in Fig. 1, where C_F^{14} corresponds to complete polymerization. Values of k_i, calculated from the half-time, are given in Table I, column 5.

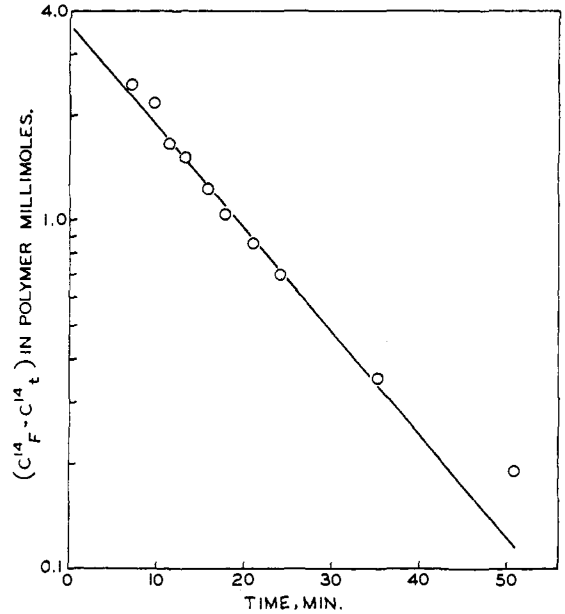

Fig. 1.—Variation of C^{14}-activity in polymer samples with time. Experimental conditions: $[(C_5H_5)_2TiCl_2]_0$, 2 millimolar; $[(CH_3)_2AlCl]_0$, 5 millimolar; temp., 15°; $p_{C_2H_4}$ 100 cm.

Chain Propagation.—Preliminary results indicated a relationship

$$R_p = dP/dt = k_p[C][m] \qquad (1)$$

where R_p is the rate of polymerization, P is the polymer formed in moles of monomer, and [C] and [m] are the concentrations of propagating metal alkyl complex and monomer, respectively.

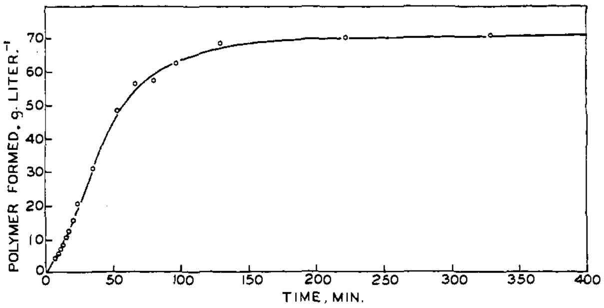

Fig. 2.—Increase of polymer yields with time. Experimental conditions same as in Fig. 1.

Values of R_p were obtained by measuring slopes of the curves of polymer weight *versus* time (*e.g.*, Fig. 2). Values of [C] were obtained from the I^{131} in polymer samples resulting from reaction of I_2^{131} with metal alkyl complexes (Fig. 3). The reaction of iodine with simple titanium and aluminum alkyls has been shown to proceed rapidly and quantitatively, and has been made the basis of a

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(7) The measurement of radioactivity was supervised by Dr. A. K. Wiebe.

(8) A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 1, 68 (1950).

(9) L. Wiesner, *Brennstoff-Chem.*, **38**, 142 (1957).

(10) M. Calvin, *et al.*, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949.

(11) Polyethylene samples were fractionated by Mrs. S. Shyluk.

(12) P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, *J. Polymer Sci.*, **31**, 453 (1958).

(13) Infrared determinations were supervised by Mr. J. A. Gailey.

TABLE I

KINETIC RESULTS

[Ti],[a] mmolar	[Al],[b] mmolar	Temp., °C.	$p_{C_2H_4}$, cm.	$(k_i)10^3$, sec.$^{-1}$	k_p, l. mole^{-1} sec.$^{-1}$	k_t, l. mole^{-1} sec.$^{-1}$	C^{14} in polymer mmoles	Efficiency of Ti. f	η_{sp}/C[c]	$(M_n)10^3$ Obsd.	$(M_n)10^3$ Calcd.	Polymer yield, mmoles	Efficiency of CH_3
2	5	30	100	6.07	12.2	8.30	2.63	1.31	0.94	8.3	9.4	3.26	1.24
2	5	30	100	5.50	11.9	9.25	2.65	1.32	1.12	10.6	...	3.76	1.42
1	2.5	30	100	4.62	15.6	8.90	1.36	1.36	1.85	18.0	18.41	1.62	1.19
2	5	15	100	1.15	4.57	1.57	3.71	1.85	1.66	15.8	15.6	4.5	1.21
4	10	15	100	1.05	5.27	(2.0)[d]	8.17	2.04	0.76	8.8	10.3	11.4	1.39
1	2.5	15	100	1.36	4.91	2.50	1.15	1.15	1.66	26.7	29.5	0.75	0.65
2	5	0	100	0.288	1.37	0.54	2.74	1.37	1.82	22.3	26.8	2.94	1.07
1	2.5	0	100	.304	1.50	.94	1.19	1.19	2.36	43.3	50.7	0.76	0.64
4	10	0	100	.253	1.66	(.49)	8.02	2.01	...	14.4	16.9	11.7	1.46
2	5	45	100	(14.9)	39.0	(35.4)	2.18	1.09	0.5	10.0	8.05	2.4	1.10
2	5	60	100	...	...	...	1.79	0.89	0.5	7.3	...	2.85	1.59
1	5	30	100	1.23	15.1	5.80	3.27	3.27	1.17	15.8	16.2	3.59	1.10
0.5	5	30	100	0.304	12.8	3.97	3.63	7.26	1.09	23.7	21.6	4.77	1.31
2.5	2.5	30	100	4.62	19.0	8.50	1.41	0.56	0.97	14.1	14.3	1.48	1.05
2	5	15	255	1.00	5.12	2.43	3.96	1.98	...	24.3	31.3	4.8	1.22
1	2.5	30	255	5.02	14.3	9.9	1.68	1.68	1.84	27.0	27.1	2.09	1.24
0.5	2.5	30	255	1.36	11.8	4.7	2.19	4.38	1.32	30.5	38.9	1.53	0.70
.125	2.5	30	255	...	...	...	0.76	6.10	2.10	41.7	...	0.58	0.76
.5	1.25	30	175	5.25	15.0	9.66	0.69	1.38	1.74	33.8	31.5	0.75	1.08
.25	0.625	15	175	1.05	6.1	2.25	0.66	1.32	5.76	111	91.3	0.56	0.85
1	2.5	30	51.7	3.85	13.5	9.0	1.30	1.30	1.21	9.0	9.0	1.69	1.30
												Av.	1.07
												S.D.	0.27

[a] $[(C_5H_5)_2TiCl_2]_0$. [b] $[(CH_3)_2AlCl]_0$. [c] Specific viscosity measured at 0.1% in Decalin at 135°. [d] Values in parentheses were extrapolated.

method of analysis for these metal alkyls.[14] Furthermore, prior quenching of polymer samples with butanol followed by addition of I_2^{131}, either in the dark or under illumination, resulted in only background activity. This indicates that incorporation of I^{131} by reactions involving polymer unsaturation is negligible.

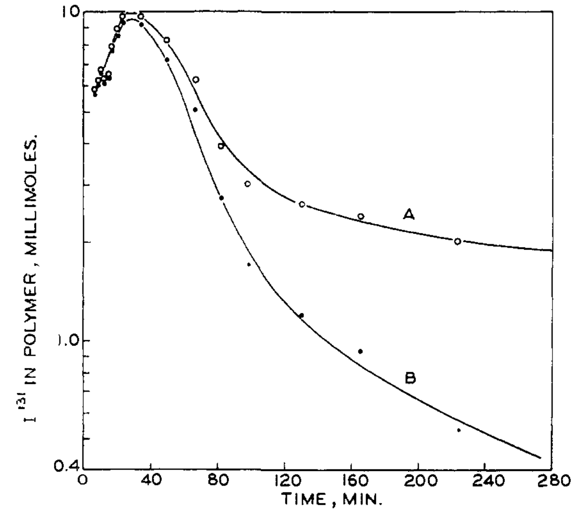

Fig. 3.—Variation of I^{131} activity in polymer samples with time. Experimental conditions the same as in Fig. 1.

The I^{131} content of the polymer is appreciable even after the polymerization is virtually completed. Thus, there are present some polymeric species which, although not propagative, still react with iodine. The amount of such species present at any time was found to increase with increasing Al to Ti ratio in the catalyst mixture. As will be pointed out in a later section, their concentration should be directly proportional to the extent of polymerization. Therefore, a correction was applied by subtracting from the I^{131} content in the polymer at time t (Fig. 3, curve A) a quantity

$$(I_T^{131}) \frac{(\text{weight of polymer at time } t)}{(\text{weight of polymer at time } T)}$$

where (I_T^{131}) was the I^{131} in the polymer at time T when polymerization was completed. The corrected curve (Fig. 3, curve B) represents the actual concentration, [C], of propagating metal polymeric alkyls. The agreement found between calculated and determined values of $\bar{M}_n$, to be discussed in a later section, indicates this equivalence to be valid.

Values of k_p were calculated by using a constant R_p, over the relatively straight portion of the polymerization curves, *e.g.*, between t = 15 and 50 min. in Fig. 2, and a relatively constant [C] over the corresponding section in Fig. 3, curve B. They are summarized in Table I, column 6. These values are only slightly affected (less than 10%) by the correction for the nonpropagating sites.

Use of corrected values for [C] led to a constant value of k_p throughout the entire reaction; without this correction the calculated values of k_p increased with the extent of polymerization.

Chain Termination.—At a fixed temperature and monomer pressure, the polymer molecular weight depends mainly upon the catalyst concentration. Preliminary experiments demonstrated an inverse relationship between the two, indicating a bimolecular termination mechanism. Indeed, the plot of

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(14) R. D. Mair, private communication.

the reciprocal of [C] of the decaying portion of Fig. 3, curve B *versus* time was found to be linear (Fig. 4). Values of k_t (Table I, column 7) were calculated according to the kinetic expression for chain termination

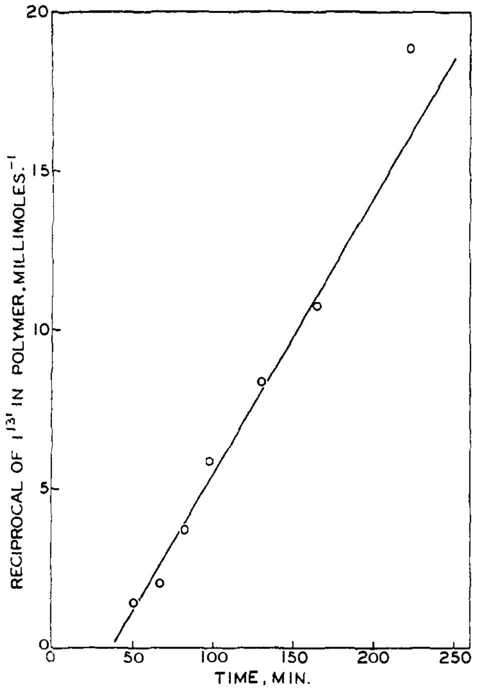

Fig. 4.—Second-order decrease of I^{131} activity in polymer samples. Experimental conditions the same as in Fig. 1.

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_t[\mathrm{C}]^2 \qquad (2)$$

The averaged values of the rate constants of various processes at several temperatures are given in Table II.

TABLE II

AVERAGE VALUES OF RATE CONSTANTS

Temp., °C.	k_i^a 10^3, sec.$^{-1}$	k_p, l. mole^{-1} sec.$^{-1}$	k_t,^{a} l. mole^{-1} sec.$^{-1}$
0	0.282 ± 0.26 (3)^b	1.50 ± 0.15 (3)	0.49 ± 0.05 (2)
15	1.12 ± .13 (5)	5.19 ± 0.57 (5)	2.19 ± .43 (4)
30	4.99 ± .71 (7)	13.6 ± 1.4 (10)	9.07 ± .58 (7)
45	...	39.0 (1)	...

^{a} For Al to Ti ratio ≤2.5. ^{b} Number of determinations.

Catalyst Efficiency.—The efficiency of methyl was determined as the number of polymer molecules produced per $C^{14}H_3$ found in the polymer. They are listed in Table I, column 14. Also, a comparison was made between the number of $C^{14}H_3$ groups which initiated polymerization and the number of $(C_5H_5)_2TiCl_2$ molecules in the reaction mixture. This ratio, f, which is called the efficiency of titanium, is given in Table I, column 9.

Energies of Activation.—The energies of activation were obtained graphically from the Arrhenius plots shown in Fig. 5. The values are 15.5, 12.2, and 16.4 kcal. mole^{-1}, respectively, for chain initiation, propagation and termination.

Calculation of Number-average Molecular Weight.—The kinetic data obtained in this work enabled calculation of $\bar{M}_n$s for comparison with those determined from fractionation of polyethylenes. Let us consider first the case where $f \leq 1$. The individual processes of polymerization may be represented by the equations

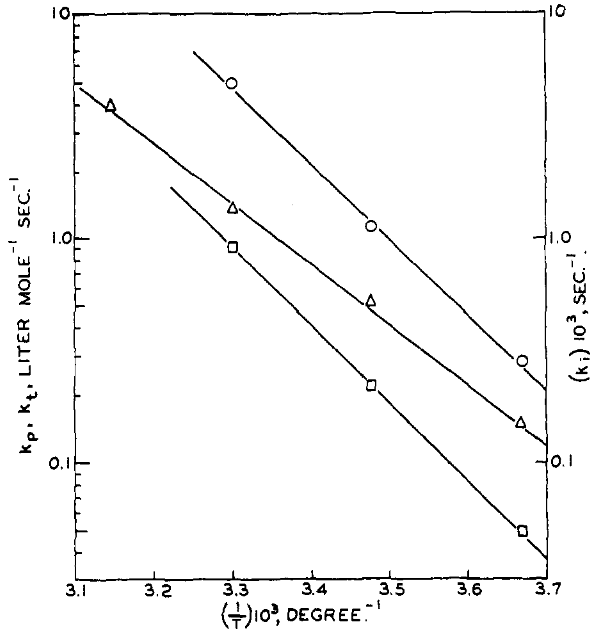

Fig. 5.—Arrhenius plots: ○, k_i; △, k_p; □, k_t.

$$(C_5H_5)_2TiCl_2 + (CH_3)_2AlCl \longrightarrow (C_5H_5)_2TiCl_2\cdot(CH_3)_2AlCl \text{ fast} \qquad (3)$$

$$(C_5H_5)_2TiCl_2\cdot(CH_3)_2AlCl \xrightarrow{k_i} [AT](CH_3) \qquad (4)$$

$$[AT](CH_3) + nC_2H_4 \xrightarrow{k_p} [AT](C_2H_4)_n(CH_3) \qquad (5)$$

$$2[AT](C_2H_4)_n(CH_3) \xrightarrow{k_t} \text{polymers} \qquad (6)$$

[AT] is the propagating metal alkyl complex, the concentration of which is denoted as [C]. The mechanism of these reactions will be discussed in a later section. The change of [C] with time is

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_i[\mathrm{T}] - k_t[\mathrm{C}]^2 \qquad (7)$$

where $[\mathrm{T}] = [(C_5H_5)_2TiCl_2]$. Equation 7 was solved[15] to give

$$[\mathrm{C}] = x[k_i[\mathrm{T}]_0/k_t]^{1/2}\left[\frac{I_1(a_0)K_1(a_0x) - K_1(a_0)I_1(a_0x)}{I_1(a_0)K_0(a_0x) + K_1(a_0)I_0(a_0x)}\right] \qquad (8)$$

where

$$a_0 = 2[k_t[\mathrm{T}]_0/k_i]^{1/2} \qquad (9)$$

$$x = \exp\,[-k_it/2] \qquad (10)$$

and I_0, K_0 and I_1, K_1 are hyperbolic Bessel functions of zero and first order, respectively. Substitution of equation 8 into (1) and integration gives

$$P = \frac{k_p[\mathrm{m}]}{k_t}\ln\left[\frac{I_1(a_0)K_0(a_0x) + K_1(a_0)I_0(a_0x)}{I_1(a_0)K_0(a_0) + K_1(a_0)I_0(a_0)}\right] \qquad (11)$$

The number-average molecular weight is equal to

$$\bar{M}_n = (P)(28)/N \qquad (12)$$

where N is the total number of polymer molecules at time t, including terminated and active, and is given by

$$N = [T]_0(1 - x^2) \text{ for termination by dispropn.} \qquad (13)$$

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[15] The solutions to differential equations were obtained by Dr. W. E. Davis; see also J. Y. Chien, THIS JOURNAL, **70**, 2256 (1948).

or

$$N = \frac{[T]_0(1 - x^2) + [\mathrm{C}]}{2} \text{ for termination by combn.} \quad (14)$$

Better agreement between calculated and determined values of $\bar{M}_n$ are obtained when disproportionation is taken as the termination mechanism. From equations 11, 12 and 13

$$M_n = \frac{k_p[m](28)}{k_t[\mathrm{T}]_0(1 - x^2)} \ln \left[\frac{I_1(a_0)K_0(a_0x) + K_1(a_0)I_0(a_0x)}{I_1(a_0)K_0(a_0) + K_1(a_0)I_0(a_0)}\right] \quad (15)$$

for $f \leq 1$. However, f is greater than unity in most of the reactions studied. The correct expression for calculation of $\bar{M}_n$ in these cases would be

$$M_n = \frac{k_p[m](28)}{k_t[T]_0(1 - x^2)f} \ln \left[\frac{I_1(a_0)K_0(a_0x) + K_1(a_0)I_0(a_0x)}{I_1(a_0)K_0(a_0) + K_1(a_0)I_0(a_0)}\right] \quad (16)$$

The calculated $\bar{M}_n$ values are summarized in Table I, column 12, along with the measured values. Variations of both calculated and measured values of $\bar{M}_n$ with time of polymerization are shown in Figs. 6 and 7. The agreement between the calculated and the measured $\bar{M}_n$ is better than 30% in all cases.

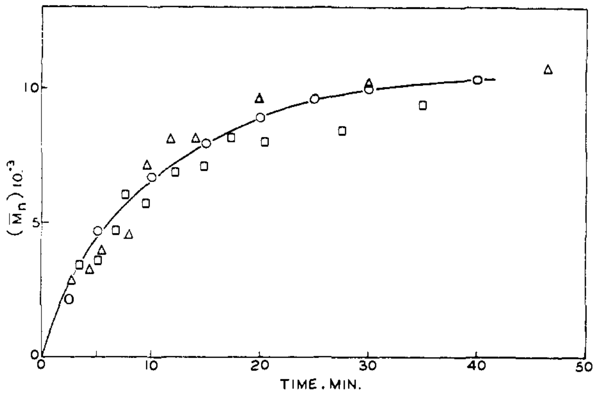

Fig. 6.—Variation of $\bar{M}_n$ with time. Experimental conditions: $[(C_5H_5)_2TiCl_2]_0$, 2 millimolar; $[(CH_3)_2AlCl]_0$, 5 millimolar; temp., 30°; $p_{C_2H_4}$, 100 cm. ○, $\bar{M}_n$ calculated from $k_i = 5.79 \times 10^{-3}$ sec.$^{-1}$, $k_p = 12.0$ l. mole^{-1} sec.$^{-1}$, $k_t = 8.77$ l. mole^{-1} sec.$^{-1}$; □ and △, $\bar{M}_n$ found for duplicate experiments.

Earlier it was assumed that the corrected I^{131} content of the polymer was a direct measurement of the instantaneous concentration of propagating chains, [C]. In view of the agreement found between the calculated and the measured values of $\bar{M}_n$, a limit for the validity of this assumption may be established. If the two quantities, $[I^{131}]$ and [C], differ by a proportionality factor, y, *i.e.*, $[I^{131}] = y[\mathrm{C}]$, then the value of y must lie within the limit $0.85 < y < 1.15$.

Unsaturation in Polymer.—The infrared determinations showed that in all the polymers obtained, the *trans*-vinylene content was either not detected or negligible. For the 14 experiments at 100-cm. monomer pressure, the average vinyl and vinylidene contents were found to be 0.44 ± 0.17 and 0.15 ± 0.08 per polymer, respectively. For polymers obtained from experiments at ethylene pressures of 175 and 255 cm., their unsaturation contents showed excessive scattering which defied any satisfactory explanation.

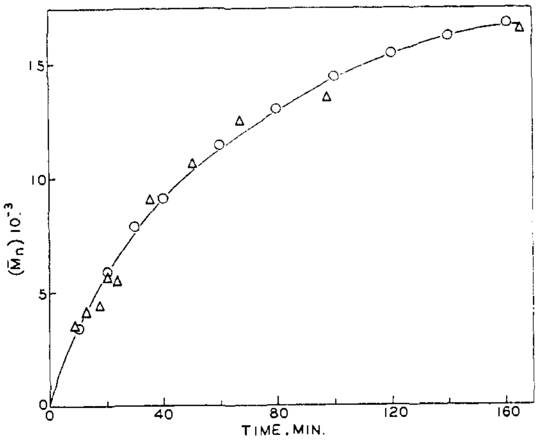

Fig. 7.—Variation of $\bar{M}_n$ with time. Experimental conditions same as in Fig. 1. ○, $\bar{M}_n$ calculated from $k_i = 1.05 \times 10^{-3}$ sec.$^{-1}$, $k_p = 4.57$ l. mole^{-1} sec.$^{-1}$, $k_t = 1.57$ l. mole^{-1} sec.$^{-1}$; △, $\bar{M}_n$ found.

Discussion of Results

The chain initiation process is believed to involve a fast reaction of the catalyst components to form a complex which is catalytically inactive. Spectrophotometric results in this Laboratory[16] showed that upon mixing the solutions of $(C_5H_5)_2TiCl_2$ and $(CH_3)_2AlCl$, a complex was formed instantaneously. This complex, in turn, formed the active species with a measureable rate. This mechanism agrees with the observation that the rate of initiation is dependent only upon the initial concentration of $(C_5H_5)_2TiCl_2$.

It was found that k_i is dependent upon the Al to Ti ratio, initiation being slower at higher ratios. Therefore with excess of $(CH_3)_2AlCl$, the active species may be in equilibrium with one or more inactive species.

The nature of the active species, which is equivalent to the propagating species, has been the subject of much speculation. The active species is undoubtedly a complex containing both Al and Ti, the latter in its tetravalent state.[17] The Al and Ti are probably bridged through one or more CH_3 and/or Cl groups.[18] Three possible types of structures can be written for the active species, differing mainly in the location of the propagating

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(16) W. P. Long, private communication.

(17) More discussion on the structure of the active species in the catalyst system, bis-(cyclopentadienyl)-titanium dichloride–alkylaluminum complexes, is presented in another paper, D. S. Breslow and N. R. Newburg, This Journal, **81**, 81 (1959).

(18) Both *Ti* and *Al* have available low energy orbitals which are necessary for the formation of the bridge-type delocalized bonds. Thus, $(CH_3)_3Al$ was found to be dimeric both in the liquid and in the vapor phase.[19] $(C_2H_5)_3Al$ and $(nC_3H_7)_3Al$ were also found to be dimeric in benzene solution.[20] For $(CH_3)_2AlCl$, Raman spectra data indicated a dimeric structure with exclusively methyl bridges.[21] Preliminary results on the crystallographic study of $(C_5H_5)_2TiCl\cdot(C_2H_5)_2AlCl$ where the Ti is trivalent indicated bridging through Cl only.[22]

(19) P. H. Lewis and R. E. Rundle, *J. Phys. Chem.*, **21**, 986 (1953).

(20) K. S. Pitzer and H. S. Gutowsky, This Journal, **68**, 2204 (1946).

(21) G. P. Vander Kelen and M. A. Herman, *Bull. soc. chim. Belges*, **65**, 362 (1956).

(22) G. Natta, P. Corradini and I. W. Bassi, This Journal, **80**, 757 (1958).

alkyls. The alkyls may be (1) bridged always between Ti and Al, (2) bonded to Ti and (3) bonded to Al. The first two structures are preferred because several examples of catalyst systems consisting of titanium compounds only are known[23] such as $(CH_3)TiCl_3$, $(CH_3)TiCl_3–TiCl_3$, $(C_5H_5)_2Ti(C_6H_5)_2–TiCl_4$ and others. Then, the functions of aluminum alkyl are twofold. First of all, it alkylates the Ti; secondly, it acts as an acid to create electron deficiency in Ti which promotes the complexing of ethylene with Ti.

The propagation step can be visualized as complexing of ethylene through overlapping of its π-electrons with the metal orbitals, probably the 3d-orbitals of Ti, followed by shifting of the alkyl group from Ti to ethylene and conversion of the bonding of the latter to Ti to a σ-bond. These steps are postulated to take place simultaneously in a concerted mechanism.

The values of k_p remained constant for $(C_5H_5)_2TiCl_2$ concentrations from 0.25 to 4 millimolar, Al to Ti ratio from 1 to 20, and monomer pressures from 52 to 255 cm. Thus, it is justified to write the rate of propagation as equation 1; k_p at 30° is 13.6 ± 1.4 l. mole^{-1} sec.$^{-1}$. This value is comparable to some of the slower free radical polymerizations. Values of k_p reported for butyl acrylate[24] and *p*-methoxystyrene[25] at 30° are 14 and 21 l. mole^{-1} sec.$^{-1}$, respectively.

The activation energy for the propagation step is 12.2 kcal. mole^{-1}. The entropy of activation for propagation is calculated to be -14.9 cal. degree^{-1} mole^{-1}, assuming a value of unity for the transmission coefficient. The values of E_p for free radical polymerizations are usually about 7 kcal. mole^{-1}. A value of about 8 kcal. mole^{-1} was estimated[26] for the diazomethane-initiated ethylene polymerization. The high E_p found in this system is accompanied by a high frequency factor which is calculated to be 10^{10} l. mole^{-1} sec.$^{-1}$. The values of A_p for free radical polymerizations ranged from 10^6 to 10^8 with notable exception in the vinylidene chloride system. The high frequency factor may be attributed to the ability of the catalyst site, upon collision with a monomer, to hold the latter *via* π-bonding until the transition state complex is formed. It is also likely that the configuration of this complex enables easier transfer of energies among various vibrational modes of freedom than in the case of free radical polymerization.

The over-all activation energy may be calculated as $1/2\ (15.5) + 12.2 - 1/2\ (16.4) = 11.75$ kcal. mole^{-1}. The apparent over-all activation energies for thermal and diazomethane-initiated ethylene polymerizations are 43.5[27] and 34.8[28] kcal. mole^{-1}, respectively. It is interesting to note that Natta and co-workers[29] have reported an over-all activation energy of $11.5 \pm 0{,}5$ kcal. mole^{-1} for the polymerization of propylene using the catalyst system, $TiCl_3–Al(C_2H_5)_3$.

The tracer technique made it possible to determine directly the efficiency of methyl in initiating polymerizations. Whereas there was considerable scattering, on the average each methyl group which initiated a chain gave one polymer molecule (Table I, column 14, average 1.07 ± 0.27). This precludes chain transfer processes in this system which do not require a new methyl group. One such reaction would be transfer with monomer to give a metal–ethyl complex and a polymer with a vinyl end-group. The former would initiate a new chain, resulting in more than one polymer molecule from each labeled methyl. Similarly, transfer with the solvent is unimportant for the same reasoning. Another such process is one whereby the metal polymer alkyl dissociates to a metal hydride which then initiates a new chain.

Table I, column 9, shows that the value of *f*, the number of polymer molecules formed per $(C_5H_5)_2TiCl_2$ present, is usually greater than one, and that it increases with increase of Al to Ti ratio. Therefore, Ti(IV) must have participated in promoting initiation and propagation of more than one polymer molecule before its reduction to Ti(III) in termination. The net process may be written as the exchange of a methyl group with a growing polymeric alkyl group, *i.e.*

$$[AT]R + (CH_3)_2AlCl \longrightarrow [AT](CH_3) + (CH_3)RAlCl \qquad (19)$$

and

$$[AT](CH_3) + nC_2H_4 \longrightarrow \text{propagation} \qquad (5)$$

$(CH_3)RAlCl$ is probably the non-propagating species found in the I^{131} determinations, and its concentration should be directly proportional to the extent of polymerization.

The chain termination is second order with respect to the concentration of active species. The values of k_t decrease with increase of Al to Ti ratio. This may be explained if the excess aluminum alkyl retards termination by occupying the available Ti orbitals which are otherwise utilized to form the transition state complex for termination. In contrast, values of k_p remained constant in the range of Al to Ti ratios studied. This could be a difference only in degree. It is conceivable that at very high Al to Ti ratios, k_p would also show some decrease.

In the bimolecular termination, Ti(IV) is reduced to Ti(III). Both crystalline $(C_5H_5)_2TiCl\cdot(C_2H_5)_2AlCl$[18] and $(C_5H_5)_2TiCl\cdot(C_2H_5)AlCl_2$[15] have been isolated as the products of reaction between $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_3$ and $(C_2H_5)_2AlCl$, respectively. These workers found that the Ti(III) complexes were not catalysts for ethylene polymerization under mild conditions of room temperature and atmospheric pressure of ethylene.

Disproportionation is preferred over combination as the termination mechanism because (1) the polymer contains one $C^{14}H_3$ group, (2) there is about 0.5 C=C group in each polymer, and (3) better agreement between calculated and measured $\bar{M}_n$ values is obtained when bimolecular disproportionation termination is postulated.

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[23] Belgium Patents 553,477 and 559,048 (1957); G. Natta, P. Pino, G. Mazzanti and R. Lanzo, *Chim. e ind.* (*Milan*), **39**, 1032 (1957).

[24] H. W. Melville and A. F. Bickel, *Trans. Faraday Soc.*, **45**, 1049 (1949).

[25] R. W. E. Axford, *Proc. Roy. Soc.* (*London*), **A197**, 374 (1949).

[26] G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, N. Y., 1954, p. 131.

[27] H. H. Storch, THIS JOURNAL, **57**, 2598 (1935).

[28] F. O. Rice and D. H. Sickman, *ibid.*, **57**, 1384 (1935).

[29] G. Natta, I. Pasquon and E. Giachetti, *Makromol. Chem.*, **24**, 258 (1957).

The values of k_t in this system are several orders of magnitude lower than those found in radical polymerizations, which are usually about 10^7 l. mole^{-1} sec.$^{-1}$, yet polymers of relatively low molecular weights are produced. The reason for this is apparent when the concentrations of growing chains are compared. At maximum rate of polymerization, there are about 10^{-3} M of growing chains in this system in contrast to 10^{-8} M for radical polymerizations. Therefore, the actual rate of termination in this system is a hundred- to a thousand-fold faster than the free radical systems, leading to polymers of considerably lower molecular weights.

It is ambiguous to discuss the lifetime of a growing chain in a non-steady state system with bimolecular termination. Nevertheless, it is interesting to illustrate the order of magnitude of the lifetime of a growing chain in a particular polymerization, *i.e.*, the one used earlier as an example for calculations. Thus, it took 24 min. to reduce the concentration of the growing chain from 0.5 millimolar to 0.25 millimolar. Of course, the average lifetime increases with decrease of concentration and is dependent upon all the other variables which change the value of k_t.

In the catalyst system used by Ludlum, Anderson and Ashby,[30] the growing sites were demonstrated to be very longlived. The stability could be attributed to the lower valence state of Ti. Herman and Nelson[31] suggested that the alkyls of Ti(II) are relatively stable. In addition, their catalyst system is heterogeneous, in which case bimolecular termination is necessarily more difficult.

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[30] D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

[31] D. F. Herman and W. K. Nelson, *ibid.*, **75**, 3877, 3882 (1953).

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[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Anomalous pK_a Values of Some Substituted Phenylethylamines[1]

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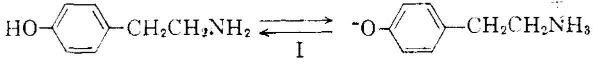
The pK_a values of some substituted phenylethylamines having pressor activity were determined. The seemingly anomalous lower pK_a values for some secondary amines in contrast to the corresponding primary amines are discussed. Some of the physiological consequences are briefly considered.

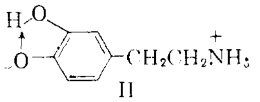
During an investigation of methods of separation and determination of arterenol (nor-epinephrine) and epinephrine, it was found that this pair of primary and secondary amines had the same pK_a value, within the limits of experimental error. This unanticipated result led to the determination of pK_a values for other pairs of pressor phenylethylamines listed in Table I. Two pairs of primary amine and corresponding N-methylamine are reported in which the primary amine has a greater pK_a value than the secondary amine. An explanation of the observed values is given below.

The Primary Amines.—The parent compound for this series, 2-phenylethylamine, has a pK_a value of 9.78. The substitution of a p-hydroxyl group in the benzene ring lowers the pK_a to 9.22. Since an inductive effect in this case would have to operate through an ethylene chain the more likely cause of decreased base strength may be attributed to zwitterion formation (I).

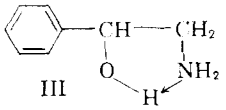


I

The further decrease in pK_a to 8.93 which results when a second hydroxyl group is introduced in the m-position (II) can be explained in terms of an increased opportunity for zwitterion formation and stabilization of the zwitterion by hydrogen bonding.



II



III

If in the parent compound a benzylic hydrogen is replaced by an hydroxyl group, a pK_a value of 8.90 is observed which is lower than that of either I or II. *A priori* this lowered basicity may be due to the inductive effect of the hydroxyl group or the presence of hydrogen bonding (III).

The observed hydrogen bonding in the ethanolamines[2] would favor this latter view. It is interesting that this effect is of greater importance in lowering basicity than zwitterion formation.

When both a p-hydroxyl group and a benzylic hydroxyl group are present (IV). the observed pK_a is 8.81. Since the inductive effect of a p-hydroxyl group would tend to develop a fractional positive charge on the benzylic carbon atom, which in turn increases the acidity of the benzylic hydroxyl group, it is clear that the resulting strengthening of the hydrogen bridge would further reduce the basicity of the nitrogen atom.

This concept of hydrogen bond strengthening by the operation of an inductive effect is supported

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[1] Presented before the Division of Medicinal Chemistry at the American Chemical Society, 134th National Meeting, Chicago, Ill., September 8, 1958.

[2] E. D. Bergmann, E. Gil-Av and S. Pinchas, THIS JOURNAL, **75**, 68 (1953).