Monomer–Polymer Interactions. Tracer Studies Involving Homogeneous Ziegler Catalysis

Gerald I. Keim,* Donald L. Christman, Leo R. Kangas, and Shirley K. Keahey

Pine and Paper Chemicals, Research Division, Hercules Incorporated, Wilmington, Delaware 19899. *Received November 20, 1971*

ABSTRACT: An ethylene–propylene copolymer containing 38 wt % propylene was prepared using a soluble catalyst made *in situ* from $VOCl_3$ and $Et_3Al_2Cl_3$ containing ^{14}C under conditions of rigid control of reaction variables. This polymer has been fractionated on a sand column into 15 fractions; each fraction was characterized by determining $\bar{M}_n$ (from osmometry), $[\eta]$, $\bar{M}_w$ by light-scattering measurements, radioactive content, and $\bar{M}_w/\bar{M}_n$ by GPC. From these data, the following conclusions have been made. (1) The equation relating intrinsic viscosity to $\bar{M}_w$ was found to be $[\eta] = (4.07 \times 10^{-4})\bar{M}^{0.74}$. Values for $\bar{M}_v$ and $\bar{M}_w$ are nearly identical (probably within 10%) with a polydispersity of the fractions less than 3 and $\bar{M}_w$ from 30,000 to 1,000,000. (2) Polymer chains with $\bar{M}_n < 75{,}000$ contained on the average less than one radioactive site. Chains with $\bar{M}_n > 75{,}000$ contained more than one radioactive site. The overall average number of radioactive tags was 0.9 per chain. These data indicate that monomer probably exchanges with growing chains containing tagged groups, causing radioactive monomer to be released into the reaction medium and nontagged growing chains to be initiated. The radioactive monomer so released can be reincorporated into growing chains; when these chains already contain a radioactive center, the resulting polymer will contain more than one ^{14}C. (3) The productivity of the catalyst was determined to be about 1.4. That is, slightly more than one chain was initiated per catalyst site on the average.

Ziegler catalysts have been used extensively for the preparation of high molecular weight polymers from α-olefins at moderate temperatures and pressures. Included in these polymers are the amorphous copolymers prepared from ethylene and propylene. Numerous articles regarding their preparation and properties have appeared in the literature.[1–3] As pointed out in a previous paper,[4] the preparation of a reproducible, homogeneous, amorphous copolymer involves strict control of reaction conditions and catalyst. A homogeneous catalyst permits such control much more readily than a heterogeneous one; thus the homogeneous catalyst prepared *in situ* from the reaction of a soluble vanadium compound and an aluminum alkyl has been the choice of many workers in the field. There has been considerable speculation about the nature of the active species, the initiation, propagation, and termination reactions, and the productivity of the catalyst, *i.e.*, the number of polymer chains initiated per catalyst site. It was thought that the use of an aluminum alkyl containing ^{14}C in preparing the catalyst would result in the "tagging" of polymer chains; fractionation of the resulting polymer and measurements of the radioactive content and number-average and weight-average molecular weights of the fractions would provide answers to several of these questions. Moreover, these data would permit a better definition of the relationship between molecular weight and intrinsic viscosity than is possible with whole polymer.

Such a study was done in our laboratories and is the subject of the present paper.

Specifically, the polymer chosen for investigation was an ethylene–propylene copolymer containing 38 wt % propylene. It was prepared in a hydrocarbon solvent using a catalyst prepared *in situ* from the reaction of vanadyl chloride ($VOCl_3$) and ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) in which the ethyl groups contained ^{14}C. The polymer was fractionated using the method of Henry[5] to give 15 fractions. Light-scattering measurements yielded a value for $\bar{M}_w$, while $\bar{M}_n$ was determined by osmometry. The radioactivity of each fraction was also determined.

(1) C. A. Lukach and H. M. Spurlin in "Copolymerization," Vol. 18, G. Ham, Ed., Interscience, New York, N. Y., 1964, pp 115–147.
(2) G. Bier, *Angew. Chem.*, **73**, 186 (1961).
(3) G. Natta, G. Sarton, A. Valvassori, and G. Crespi, *Hydrocarbon Process., Petrol. Refiner.*, **41** (8), 103 (1962).
(4) D. L. Christman and G. I. Keim, *Macromolecules*, **1**, 538 (1968).
(5) P. M. Henry, *J. Polym. Sci.*, **36**, 3 (1959).

Discussion of Results

Tagging of Chains. Initially, it was assumed that every polymer chain would contain at least one radioactive center. This would result from the alkylation of a vanadium atom by the radioactive alkyl used. That is, the initiation step in the polymerization could be expressed by

$$Et^*_3Al_2Cl_3 + VOCl_3 \longrightarrow Cl_2AlO\overset{Cl}{\overset{|}{Al}}Et^* + VCl_3 + CH_2{=}\overset{*}{C}H_2 + \overset{*}{C}H_3CH_3 \quad (1)$$

$$VCl_3 + Et^*_3Al_2Cl_3 \longrightarrow Cl_2VEt^* + Et^*_2Al_2Cl_4 \quad (2)$$

The actual reactions are more complicated because the various species are undoubtedly complexed. If they were not, the vanadium compounds would precipitate, whereas the polymerization appeared to be completely homogeneous.

The propagation step is pictured as proceeding by the insertion of a monomer unit between the alkyl group and the vanadium atom

$$Cl_2VEt^* + n RCH{=}CH_2 \longrightarrow Cl_2V(CH_2CHR)_nEt^* \quad (3)$$

Termination by disproportionation would complete the chain, as shown in

$$2Cl_2V(CH_2CHR)_nEt^* \longrightarrow (CH_3{-}CH_2)(CH_2{-}CHR)_{n-1}Et^* + CH_2{=}CH(CH_2CHR)_{n-1}Et^* + 2Cl_2V \quad (4)$$

That this simple picture of initiation, propagation, and termination is incomplete is indicated by the data presented in Table I. If these reactions were the only ones involved, each chain should have at least one radioactive tag. Thus the determination of the radioactive content should yield a value for the number-average molecular weight, $\bar{M}_n$; this number should be identical with the value of $\bar{M}_n$ determined osmometrically. The data in Table I indicate that this is not true. The value of the ratio $\bar{M}_n(\text{osm})/\bar{M}_n(^{14}C)$ [desig-

TABLE I
ANALYSIS OF FRACTIONS

Fraction no.	Wt fraction	Wt % C_3[a]	$[\eta]$[b]	$\overline{M}_w(LS)/\overline{M}_n(osm)$	$\overline{M}_w/\overline{M}_n$ (GPC)	Corr[c] $\overline{M}_w/\overline{M}_n$	$\overline{M}_w(LS) \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$ GPC[d]	$\overline{M}_n \times 10^{-3}$ Osm	$\overline{M}_n \times 10^{-3}$ Av	Radioactivity μCi/mg $\times 10^5$	Radioactivity mmol of Et/mg	Tags per chain[e] (1)	Tags per chain[e] (2)
1	0.0059	41.2	0.17		1.89	1.68		3.42[f]			5.40	6.61		
2	0.0004													
3	0.0162		0.31		1.48	1.32	15.5[g]		10.5	10.5	3.31	4.05	0.426	0.426
4	0.0126	44.9	0.46		1.36	1.21	23.4[g]		17.2	17.2	2.31	2.83	0.486	0.486
5	0.0126	48.3	0.68	1.51	1.55	1.38	38.9	28.2	25.8	27.0	1.91	2.34	0.596	0.631
6	0.0315	45.1	0.83	1.36	1.86	1.66	49.1	29.6	36.2	32.9	1.57	1.92	0.697	0.632
7	0.0432	49.0	1.00	1.32	1.98	1.76	55.5	31.5	42.2	36.8	1.45	1.78	0.750	0.655
8	0.1134	44.1	1.34	1.40	1.67	1.49	84.0	65.4	59.8	58.1	1.24	1.52	0.908	0.883
9	0.1020	43.4	1.60	1.46	1.35	1.20	135	108	92.7	100	1.05	1.29	1.19	1.29
10	0.0520	43.0	1.93	1.53	1.43	1.28	167	130	109	120	0.94	1.15	1.26	1.38
11	0.2227	43.1	2.36	1.20	1.63	1.45	185	128	154	141	0.855	1.05	1.62	1.48
12	0.1764	42.1	3.56	1.74	1.70	1.15	443	293	255	274	0.806	0.99	2.52	2.71
13	0.0789	41.1	4.64	1.47	1.84	1.64	541	330	368	349	0.829	1.01	3.72	3.52
14	0.0943	39.4	5.14	1.75	2.41	215	645	300	368	334	0.880	1.08	3.97	3.61
15	0.0378	31.5[h]	6.84	3.53	2.91	2.59	1000	386	283	334	0.977	1.20	3.40	4.01

[a] Measured by infrared; solution in CCl_4. [b] One-point viscosity. [c] From Figure 2, true $\overline{M}_w/\overline{M}_n$ = 0.89(measured $\overline{M}_w/\overline{M}_n$). [d] $\overline{M}_w(LS)/(\overline{M}_w\overline{M}_n(GPC))$ corrected. [e] (1) based on $\overline{M}_n$(osm), (2) based on $\overline{M}_n$(av). [f] $\overline{M}_w/(\overline{M}_w\overline{M}_n(GPC))$ corrected. [g] Obtained from osmometry and GPC distribution; too low for light-scattering measurements. [h] Partially insoluble in CCl_4.

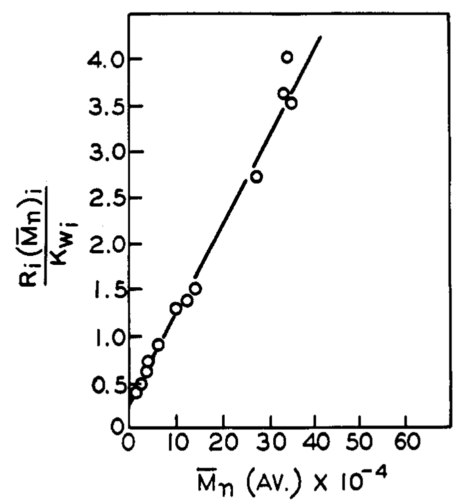

Figure 1. Tags per chain *vs.* $\overline{M}_n$. Intercept = −0.325 Et/mol; slope = −0.94 Et/g.

nated as tags per chain (1)] rises as the molecular weight increases if the $\overline{M}_n$(osm) is assumed to be correct. That is, the lower molecular weight fractions then must contain less than one radioactive center per chain on the average while those chains with $\overline{M}_n > 75{,}000$ contain more than one tag. This is shown in Figure 1.

Figure 1 was obtained as follows. It was hypothesized that a fraction x of the chains was initiated by a radioactive ethyl group and that a fraction y of the ethylene units along the chain was also labeled. The value of M_w is not required; the radioactivity (R_i) of a fraction will be given by

$$R_i = K\left(\frac{w_i}{(M_n)_i}x + w_i y\right) \quad \text{(I)}$$

where K is the radioactivity of the ethylene equivalent of the alkyl groups in the $Et_3Al_2Cl_3$ used as the original alkylating agent and w_i is the weight of the fraction. Rearrangement of (I) yields

$$\frac{R_i(M_n)_i}{Kw_i} = x + (M_n)_i y \quad \text{(II)}$$

which is the equation for a straight line. The intercept gives the average end-group labeling, while the slope measures the random incorporation. Two hidden assumptions in this treatment are: (1) there was no termination by combination and (2) there was no change in the nature of the polymer produced during the course of the polymerization.

Several reactions could explain the presence of more than one tag per chain, as, for example, cross-linking of the unsaturated chain.

$$Cl_2V(CH_2CHR)_nEt^* + CH_2{=}CH(CH_2CHR)_nEt^* \longrightarrow Cl_2VCH_2\overset{\displaystyle (CH_2CHR)_nEt^*}{\overset{|}{C}}HR(CH_2CHR)_nEt^* \quad (5)$$

Or note that eq 1 predicts the release of radioactive ethylene which can be incorporated into a growing chain

$$Cl_2V(CH_2CHR)_nEt^* + CH_2{=}\overset{*}{C}H_2 \longrightarrow Cl_2V\overset{*}{C}H_2CH_2(CH_2CHR)_nEt^* \quad (6)$$

To account for the presence of chains containing less than one tag, another reaction must be considered, perhaps the exchange of monomer with a growing chain

$$Cl_2VEt^* + CH_2{=}CH_2 \longrightarrow Cl_2VEt + CH_2{=}CH_2^* \quad (7a)$$

$$Cl_2V(CH_2CHR)_nEt^* + CH_2{=}CH_2 \longrightarrow Cl_2VEt + CH_2{=}\overset{\displaystyle R}{\overset{|}{C}}(CH_2CHR)_{n-1}Et^* \quad (7b)$$

Thus a chain could be formed with no radioactive tag, as shown by

$$Cl_2VEt + nCHR{=}CH_2 \longrightarrow Cl_2V(CH_2CHR)_nEt \quad (8)$$

The exchange reaction (eq 7) also releases ethylene or an α-olefin containing a radioactive tag into the reaction medium.

These in turn can be reincorporated into growing chains already containing a tag (eq 5 and 6).

It would be expected that reaction 5 would not occur very often for the simple reason that the concentration of the radioactive α-olefin would be very low and its reactivity close to that of propylene. The concentration of radioactive ethylene would also be low, but owing to its high reactivity it would occur readily. Under steady-state conditions, *i.e.*, when the ratio $[CH_2{=}CH_2^*]/[CH_2{=}CH_2]$ becomes constant, the chance that a growing chain would incorporate a radioactive ethylene molecule rather than a nontagged one would be directly dependent upon their relative concentrations. Thus, statistically, the longer lived the growing chain, the greater would be the chance of incorporating a tagged ethylene molecule into the chain. Thus a linear relationship between tags per chain and number-average molecular weight would be expected. This appears to be the case (Figure 1). The line does not pass through the origin, since almost half of the chains are tagged initially.

After correction for the intercept, it would be expected that doubling the molecular weight should result in a doubling of the tags per chain. The following data, where the tags per chain have been corrected for the intercept, support this suggestion ($\bar{M}_n$, tags per chain): 25,000, 0.23; 50,000, 0.46; 100,000, 0.93; 200,000, 1.875; 400,000, 3.75.

Ketley and Moyer[6] investigated side reactions in the polymerization of α-olefins by Ziegler–Natta catalysts. In the polymerization of isobutylene using a $TiCl_3$–Et_3Al catalyst, polyethylene was found in the products. These authors suggested that the ethylene was produced by the decomposition of Et_3Al, thus

$$Et_3Al \longrightarrow Et_2AlH + CH_2{=}CH_2 \qquad (9)$$

In our system, it does not appear likely that ethylene would be produced by a similar reaction, *i.e.*

$$Et_3Al_2Cl_3 \not\longrightarrow Et_2Al_2Cl_3H + CH_2{=}CH_2 \qquad (10)$$

These authors also demonstrated that reaction 11 will take

$$Et_3Al + \overset{*}{C}H_2{=}CH_2 \longrightarrow Et^*{}_3Al + CH_2{=}CH_2 \qquad (11)$$

place very slowly. Again, a similar reaction with the sesquichloride is less favored. However, such an exchange cannot be ruled out without further study.

Natta, *et al.*,[7] used a $TiCl_3$–$Et^*{}_3Al$ catalyst to polymerize propylene and found radioactive tags in the polymer. They concluded that this showed that polymerization was initiated by ethyl groups from the $Et^*{}_3Al$; Natta also used $Et^*{}_3Al$ to measure chain transfer of growing chains. Ketley and Moyer[6] point out that Natta's results are ambiguous unless reaction 11 can be eliminated as a possibility.

Fractionation and Molecular Weight. To obtain an answer to the question of how the extent of labeling varies with molecular weight, fractions obviously had to be examined. Monodisperse fractions, of course, would be most desirable. However, the method of fractionation used[5] gave fractions with $\bar{M}_w/\bar{M}_n$ ranging from 1.20 to 3.53 (Table I, column 5). Two independent methods for the determination of $\bar{M}_n$ were used, namely, osmometry and gel permeation chromatography (GPC). $\bar{M}_w/\bar{M}_n$ obtained by osmometry tends to be somewhat low; GPC values of $\bar{M}_w/\bar{M}_n$ tend to be somewhat high. Tung[8] has calculated the theoretical distribution of polyethylene fractions (obtained from repeated fractionation by GPC) from the resolution factor obtained from GPC columns and compared it with that resulting from a collection of cuts. A fraction with a GPC distribution of 1.30 actually had a distribution of 1.16. Thus, the indicated distribution was actually 12.1% too high. Similarly, Cantow, *et al.*,[9] showed that GPC gave a value for $\bar{M}_w/\bar{M}_n$ for *n*-dotetracontane which was 11.6% too high. In our work, the average GPC distribution of the fractions was 1.85 while the average of the values $\bar{M}_w$(LS)/$\bar{M}_n$(osm) was 1.66. Thus, the GPC distribution was too high by about 11%. Plotted in Figure 2, this shows good agreement with the two literature points and a constant error for $(\bar{M}_w/\bar{M}_n(GPC)/(\bar{M}_w/\bar{M}_n$ (actual)) for distributions between 1 and 2.

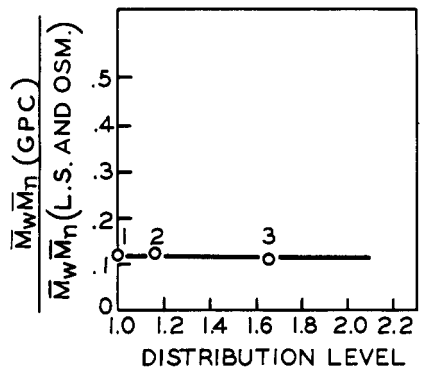

Figure 2. GPC curve broadening for various distributions: (1) Cantow, *et al.*;[9] (2) Tung;[8] (3) average of fractions below $\bar{M}_w/\bar{M}_n = 2$ in this study.

In order to obtain meaningful molecular weight values from the gel permeation separation, the standardization of the gel columns must be carried out employing narrow fractions which have the same affinity for the solvent as the sample being measured. Polystyrene standards, which are often used to calibrate the columns, can lead to gross errors when polymers of differing chemical structure are being measured. Polyethylene fractions will differ sufficiently in chain extensibility from those of polypropylene, even when employing an equalizing *P* factor of 11 and 17, respectively, that identical standardization curves are not obtained (Figure 3). Here, *P* represents the molecular weight per ångström length, considering only bond lengths and angles and assuming a fully extended linear molecule. Obviously then, the copolymer would also require a separate calibration. Dividing the light-scattering weight-average molecular weight of these fractions by 15 and plotting against retention volume puts the copolymer curve (containing 39–46% ethylene) coincident with the polyethylene calibration (Figure 3). The lower two points in the figure, being too low for a reliable light-scattering determination, were obtained by multiplying the osmotic number-average molecular weight by the GPC distribution.

Quenching with Tritiated 2-Propanol. All grab samples removed were quenched with tritiated 2-propanol. Theoretically, only those chains still attached to metal atoms (V or Al) should react and be labeled. Unless large chains were attached to the metal sites, they would be lost in the work-up. Thus, the product of the tritium activity per gram multiplied

(6) A. D. Ketley and J. D. Moyer, *J. Polym. Sci., Part A*, **1**, 2467 (1963).

(7) (a) G. Natta, G. Pajaro, L. Pasquon, and V. Stellacci, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, [8] **24**, 479 (1958); (b) G. Natta, L. Pasquon, E. Giachetti, and G. Pajaro, *Chem. Ind. (Milan)*, **40**, 267 (1958).

(8) L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 1271 (1966).

(9) M. J. R. Cantow, R. F. Porter, and J. F. Johnson, *J. Polym. Sci., Part C*, No. **16**, 13 (1967).

TABLE II
POLYMERIZATION

Sample	Time, min[a]	Al, mmol[b]	V, mmol	RSV[c]	$[\eta]$[d]	$M_w \times 10^{-5}$ [e]	Polymer,[f] g	Mol of polymer[g] $\times 10^4$	Wt % C_3[h]	Et/g $\times 10^5$ [i]	H_3/g $\times 10^7$ [i]	Et/chain	H_3/chain	Active chains, μmol/l.	Et/V	Chains/V
1	9	2.78	0.125	2.4	2.24	1.85	11.6	2.43	38.8	0.842	1.54	0.41	0.0074	0.94	0.78	1.94
2	19	3.60	0.235	3.0	2.75	2.48	21.6	3.34	39.1	0.842	1.09	0.54	0.0071	1.24	0.78	1.42
3	29	4.52	0.370	2.9	2.65	2.38	35.4	5.70	38.5	0.981	1.19	0.61	0.0074	2.20	0.94	1.54
4	39	5.40	0.495	3.1	2.82	2.62	48.0	7.02	37.8	1.08	0.92	0.74	0.0063	2.32	1.05	1.42
5	49	6.26	0.630	3.2	2.91	2.71	61.6	8.75	38.3	1.23	0.92	0.87	0.0065	2.96	1.20	1.39
6	54	6.70	0.692	3.2	2.91	2.71	67.6	9.56	38.0	1.26	0.87	0.90	0.0062	3.04	1.23	1.38

[a] From start of addition of catalyst components. [b] Includes 2.0 mmol added initially. [c] 0.1% in decalin at 135°. [d] Calculated from RSV. [e] From Figure 4. [f] Assuming 1 l. of gas (25° and 0 psig.) weighed 1.31 g. [g] Assuming $\bar{M}_w/\bar{M}_n = 3.83$. [h] By infrared analysis, pressed films. [i] Radioactive measurements.

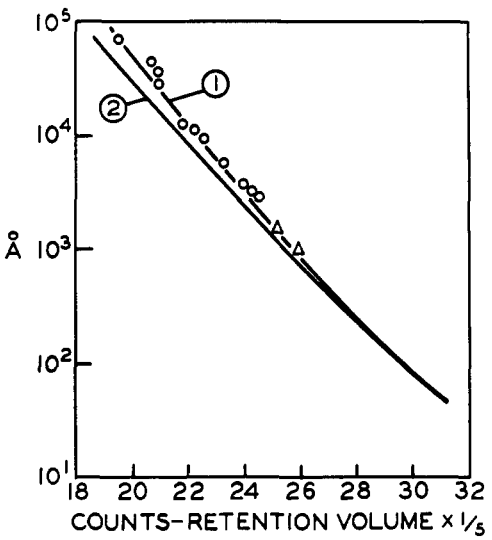

Figure 3. Gel permeation standardization: (1) polyethylene fractions, $\bar{M}_w/11$; (2) polypropylene fractions, $\bar{M}_w/17$; O, copolymer fractions, $\bar{M}_w/15$; △, osmometry, $(\bar{M}_n/15)(\bar{M}_w/\bar{M}_n)$ from GPC curve.

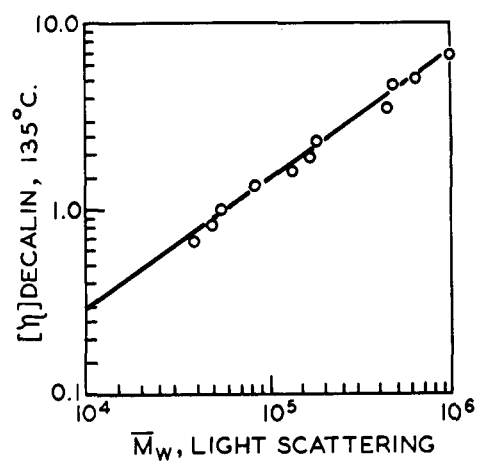

Figure 4. $[\eta]$ *vs.* $\bar{M}_w$. $[\eta] = (4.07 \times 10^{-4})\bar{M}_w^{0.74}$.

by the weight of polymer should yield the equilibrium catalyst concentration designated [c] in eq 12. (Obviously,

$$dP/dt = k_p[c][M] \quad (12)$$

this value also includes any "dead" molecules still attached to metal atoms. Therefore, the value for [c] can only be an approximation in the absence of some measurement of the latter.) Since [M] has been measured experimentally, the value of the propagation constant, k_p, should emerge when dP/dt is held constant. Unfortunately, the low level of tritium incorporated made it difficult to obtain high accuracy in the doubly labeled material. The equilibrium concentration [c] calculated as described above is shown in Table II, column 15. As can be seen, these data show a steady rise with time but at least permit an order of magnitude to be established. Under the conditions of the reaction (50°, 30 psig and dP/dt of 1 l. of gas in an ethylene:propylene ratio of 70:30 per minute for 2 l. of solvent), the value for [c] is roughly 3.0 μmol/l. of solvent. If $dP/dt = 2.05 \times 10^{-2}$ mol of monomer/(min)(l. of solvent) and [M] = 0.92 mmol/l. of solvent, then substitution into eq 14 yields a value for k_p of 1.07×10^5 l. of solvent/(min)(mol of catalyst).

TABLE III
SUMMARY OF FRACTIONATION DATA

	$[\eta]$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Column fractionation	3.0	290,000	297,600[a]	77,800[b]	3.83
GPC fractionation	2.77[c]	257,000	340,000	80,700	4.21 (3.75)[d]

[a] Calculated from $\bar{M}_w = \Sigma w_i M_i$(LS). [b] Calculated from $\bar{M}_n = 1/\Sigma(w_i/M_i)$. [c] Determined several months after initial determination; $[\eta]$ for fractions was measured at the time of each fractionation. [d] Corrected: $(\bar{M}_w/\bar{M}_n)(0.89)$ (Figure 2).

Productivity of Catalyst. The relationship between the intrinsic viscosity and $\bar{M}_w$ has been discussed and is shown graphically in Figure 4. A measurement of the specific viscosity could thus be correlated with $\bar{M}_v$ which is very close to the value of $\bar{M}_w$ for polymers with $\bar{M}_w/\bar{M}_n$ values between 2 and 4.[10] If a value for $\bar{M}_w/\bar{M}_n$ is available, then $\bar{M}_n$ can be calculated. The total weight of polymer divided by $\bar{M}_n$ thus yields the moles of polymer. This value divided by the amount of catalyst added should give a value for productivity.

The value of $\bar{M}_w/\bar{M}_n$ is given in Table III as 3.83 for the fractions studied. Thus the value for productivity of the catalyst is calculated to be in the range 1.4–1.9, as indicated for samples removed periodically during the polymerization (Table II). Strictly speaking, only sample 6 (total product) was fractionated so that it alone can be used in these calculations. However, if it is assumed that the value of $\bar{M}_w/\bar{M}_n$

(10) R. Chiang, *J. Polym. Sci.*, **36**, 91 (1959).

did not change appreciably during the polymerization, the productivity is fairly constant.

Among possible explanations for a productivity slightly greater than one chain per vanadium atom are the following: (1) reactivation of a dead catalyst site, perhaps by interaction of V^{2+} and V^{5+} species and (2) a low level of chain transfer as described by

$$Cl_2VCH_2CH_2(CH_2CHR)_nEt^* + mCH_2{=}CHR \longrightarrow Cl_2V(CH_2CHR)_m + CH_2{=}CH(CH_2CHR)Et^* \quad (13)$$

A check was made to determine whether a reasonable balance between total radioactivity introduced and that measured had been obtained. In Table II, the amount of $Et_3Al_2Cl_3$ (6.70 mmol) recorded corresponds to (6.70)(3/2) or 10.05 mmol of radioactive ethyl groups introduced. However, eq 1 and 2 predict consumption of three ethyl groups per catalyst site, with one ethyl unavailable for incorporation into the polymer since it is released as ethane. Since only 0.629 mmol of vanadium was present (see Table II or Figure 5), 2(0.692) or 1.384 mmol of ethylene* should be accounted for. As pointed out earlier, evidently 1.38 chains per vanadium atom resulted, and these chains contained 0.9 tag per chain on the average. Thus (1.38)(0.9)(0.692) or 0.86 mmol of the radioactive ethylene appeared in the polymer, or 62% of the amount predicted to be available. A small amount of unreacted radioactive ethylene would be present always if it is assumed that the $[CH_2{=}CH_2^*]/[CH_2{=}CH_2]$ ratio became constant. This would account for part of the missing 38% of radioactive ethylene.

Experimental Section

Preparation of Polymer. The apparatus used for the preparation of the polymer was a modified 1-gal Sutherland reactor.[11] The procedure was similar to that described for the preparation of uniform terpolymers described earlier.[4] Esso heptane (2 l.) dried over molecular sieves, was charged to the reactor, which was evacuated using a water aspirator. Propylene, dried by passage through a column of molecular sieves under 50 psig, was passed into the solvent with agitation until the pressure reached 0 psig. The solution was once again evacuated with a water aspirator and again saturated with propylene. The temperature was raised to 50° and additional propylene admitted until the pressure was 16.7 psig. Ethylene, also dried over molecular sieves at 50 psig, was added until the pressure reached 30 psig.

At this point, 2.0 mmol of 0.2 *M* radioactive ethylaluminum sesquichloride was added by syringe. Then the addition of 0.2 *M* radioactive sesquichloride was begun using a syringe driver; the rate was maintained at 0.43 ml/min throughout the polymerization. Simultaneously, the addition of a 0.02 *M* solution of vanadium oxytrichloride was begun using a positive displacement pump. Polymerization was noted in about 2 min, as indicated by a slight drop in pressure, which could be read to 5–10 mm by use of a tall U-tube manometer filled with mercury. Gas, composed of ethylene and propylene in a 7:3 molar ratio, was passed into the reactor at the rate of 1 l./min as measured at 25° and atmospheric pressure. The rate of addition of the solution of vanadium oxytrichloride was adjusted so that the pressure remained constant at 30 psig. Periodic readings of the volume added were taken; this is illustrated graphically in Figure 5.

A small sample of gas was removed from the head space initially and additional samples were also removed and analyzed periodically. By gas chromatography, these samples contained from 69 to 72% propylene. Liquid samples were likewise removed periodically using the dip tube which reached to the bottom of the reactor. These liquid samples were quenched with tritiated 2-propanol by shaking vigorously for 1 min. They were then washed three to four times with distilled water and the solvent was removed by evaporation in a hood. The films remaining were analyzed for propylene content and radioactive carbon and tritium content. The reduced specific viscosity (0.1% in decalin at 135°) was also determined for each sample. The data for individual samples are given in Table II.

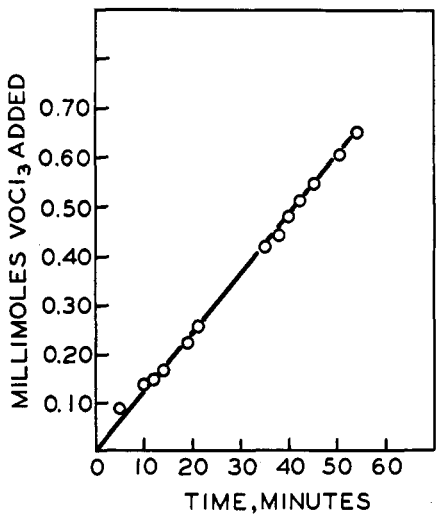

Figure 5. Addition of $VOCl_3$ *vs.* time. $d[V]/dt$ = 0.0061 mmol/min.

At the end of the polymerization, the addition of all catalyst components and gas was stopped. The solution was blown through the dip tube under autogenous pressure into a bottle containing several milliters of 2-propanol plus 10 ml of a 2% solution of 2,2-methylenebis(4-methyl-6-*tert*-butyl) sulfide to prevent oxidation. The solution was washed with distilled water until neutral and the polymer was recovered as a thin film by drying in glass trays to remove the solvent.

Fractionation of Polymer. The polymer was fractionated on a large jacketed column (5 ft × 3.5 in.) filled with sand[5] according to the following procedure. Thirty grams was dissolved in 900 ml of xylene at 130°. About 430 ml of Cellosolve (trademark, Union Carbide Corp.) were added slowly to incipient precipitation and the solution was charged to the top of the hot column (126°) and allowed to coat the support. The column was cooled slowly and washed with 3 l. of Cellosolve.

The column was reheated to 126°. Fractions were extracted with 2 l. of the suitable xylene–Cellosolve mixtures for each cut. At the end of 16 hr, the column was cooled to room temperature. It was later reheated to 126° and eluted with appropriate solvent–nonsolvent mixtures for an additional 11 hr. Inasmuch as the cuts near the middle were heavy, the first and second half of each cut were not combined in this area and were designated separately. Although they were of the same solvent composition, the molecular weight of the second half was always greater than that of the first half of the cut.

The gel permeation chromatography was done in trichlorobenzene at 130° using the Waters gel permeation chromatograph. Four columns having pore sizes 1.5×10^5–5×10^6, 10^4–10^5, 3×10^3–3×10^4, and 10^3–10^4 Å were used. Samples were injected at 0.25% concentration over a period of 90 sec. Results were computed from a calibration curve established with narrow polyethylene fractions (Figure 3).

The light scattering was done in α-chloronaphthalene at 135°. Osmometry values for $\bar{M}_n$ were measured on the Mechrolab membrane osmometer at room temperature in toluene. Diffusion through the membrane (Bac-T-Flex from Schleicher and Schuell, Keene, N. H.) occurred only in Fraction 3 ($\bar{M}_n$ = 10,500). Fractions 7 and above were analyzed with an S and S –08 membrane.

Radiochemical Counting of Samples. All counting was done

(11) J. D. Sutherland and J. P. McKenzie, *Ind. Eng. Chem.*, **48**, 17 (1956).

TABLE IV

Sample	Slow/fast[a]	Sample	Slow/fast[a]
1	1.14	4	0.72
2	1.81	5	1.43
3	0.80	6	1.15

[a] Ratio of tritium content of slowly quenched samples to that in rapidly quenched samples.

with a Packard Tri-Carb liquid scintillation spectrometer, Model 314Y. A high-voltage setting of 11 and window at 6–100 V were used for samples containing tritium; a high-voltage setting of 5 and window at 10–50 V were used for samples containing ^{14}C. For samples containing both tritium and ^{14}C, the regular ratios method[12] was used with a high-voltage setting of 6 and window settings of 5–25 and 25–80. Tritiated toluene and ^{14}C labeled benzoic acid in toluene were used as follows.

(1) Catalyst. A 1.0-ml aliquot of the catalyst solution was syringed into 200 ml of 0.5 *N* solution of iodine in anhydrous and deaerated heptane contained in a 16-oz pop bottle capped with a rubber liner and two-hole metal cap. The contents were mixed and allowed to react for 1 hr. About 10 ml of 1 *N* aqueous $Na_2S_2O_3$ was added and mixed well with the heptane layer in order to react with the excess I_2; then an aliquot of the heptane layer was placed in the liquid scintillator (4 g of 2,5-diphenyloxazole (PPO), 100 mg of *p*-bis[2-(5-phenyloxazolyl)]benzene (POPOP) diluted to 1 l. with toluene) and counted. The molar concentration of ethyl groups was obtained by hydrolysis of a separate sample and measuring the liberated ethane. The specific activity of the catalyst (μCi/mmol of C_2H_5) was calculated from the radioactivity and gas analysis values.

(2) Polymers. (a) Single-Labeled Polymers. A 25–50-mg sample was dissolved by warming in about 7.5 ml of *p*-xylene scintillator solution (4 g of PPO, 100 mg of POPOP diluted to 1 l. with *p*-xylene); 7.5 ml of scintillator gel solution (50 g of Thixcin in a scintillator solution containing 4 g of PPO, 100 mg of POPOP diluted to 1 l. with toluene) was added; and the contents were mixed and counted.

(b) Double-Labeled Polymers. The samples were prepared as described above and then counted in two windows.

Tritium Isotope Effect. A copolymer was prepared using non-radioactive ethylaluminum sesquichloride. Two samples were removed periodically. The first sample was shaken vigorously for 1 min with 0.1 ml of tritiated 2-propanol in the manner described for the radioactive copolymer. The second sample was quenched more slowly. That is, one drop (about 0.02 ml) of the tritiated alcohol was added and the solution was shaken vigorously for 60–90 sec before a second drop was added. This process was repeated until 0.3–0.4 ml had been added. Both solutions were washed three to four times with distilled water and the solvent was removed by tray drying. The tritium content in each sample was determined in millimoles of tritium per milligram of sample (area 2.2×10^{-7}–2.8×10^{-6}). In Table IV, the ratio of tritium content of the slowly quenched samples to that in the rapidly quenched samples is given for six samples removed during the course of polymerization.

Reagents. Esso heptane is a hydrocarbon cut with boiling point range 94–99°. It contains 52.5% naphthenes, 44.6% paraffins, 2.3% aromatics, and 0.6% internal olefins.

Ethylene, U. S. Industrial Chemical Co., was dried by passage through a 5-ft column, 1.875-in. o.d., of type 4A molecular sieves under 50 psig.

Propylene, Sinclair Refining Co., was purified in a manner similar to the ethylene.

Vanadium oxytrichloride was obtained from the Anderson Chemical Division of Stauffer Chemical Co., Weston, Mich. It was diluted to 0.02 *M* using Esso heptane as the diluent.

Tritiated 2-propanol was prepared by adding 0.2 ml of tritiated water (100 μCi/mg) to 75 ml of dry 2-propanol and then adding 5 g of Drierite. It was then allowed to stand overnight in a tightly capped bottle. The alcohol was decanted and distilled and the fraction boiling at 80.5–81.0° was collected. It was stored in a dry bottle closed with a serum cap and had a specific radioactivity of 62.4 μCi/mmol of H.

Ethylaluminum sesquichloride was prepared by Dr. J. C. W. Chien from aluminum and radioactive ethyl chloride using a high-vacuum line. It was diluted to the desired concentration using Esso heptane. It had a specific radioactivity of 0.816 μCi/mmol of C_2H_5 and analysis showed 0.20 mol of Al, 0.29 mol of Cl, and 0.28 mol of C_2H_5.

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(12) Operation Manual for Packard Tri-Carb Liquid Scintillation Spectrometer, 1959.