

Properties of Vinyl Chloride-Propylene Copolymers Prepared by Incremental Feed and Batch Feed Procedures

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Synopsis

A procedure is described for preparation of uniform-composition copolymers of vinyl chloride-propylene, polymers whose composition does not vary as a function of polymer conversion. Inherent viscosity (IV) and melt flow (MF) properties of these resins were determined. These were related to the propylene content ($\%P_B$) of the polymer. A linear relationship was found for IV versus $\%P_B$ and log MF versus $\%P_B$. Variation in copolymer composition as a function of conversion for batch-copolymerized vinyl chloride-propylene (VCM-P) system were calculated using established reactivity ratios. These values of $\%P_B$ at different conversions were used to predict the MF and IV values for batch-copolymerized VCM-P systems at different conversions. Experimental verification of these predictive values were made. Close agreement was found for predicted and experimentally determined MF values at different conversions. Unusual effects were observed between the predictive and experimentally determined IV values at different conversions.

INTRODUCTION

Composition of copolymers formed from comonomers of widely different reactivity ratios change during the course of a copolymerization.¹ As a consequence, there are changes in physical properties of copolymers dependent on the extent of conversion.² Variations in composition are not observed in several special cases, such as polymer azeotropes,³ charge transfer copolymers,⁴ copolymers formed at constant comonomer feed situations.⁵

Buning et al.⁶ examined copolymers of vinyl chloride (VCM) and propylene (P) and observed that polymer properties changed with conversion. Copolymers derived from batch-polymerized VCM-P systems were examined to determine polymerization factors which control MF and IV properties of the copolymers. The variation in comonomer composition at different conversion is the principle cause for changes in MF and IV properties at different conversions.

A procedure which gives VCM-P copolymers of uniform composition was developed from a polymerization system described by Thomas and Hinds.⁵ Thomas and Hinds studied copolymers of vinyl chloride and vinyl acetate. They reported that a copolymer of uniform composition could be prepared when the equilibrium vapor pressure of the unreacted monomers was maintained at a constant value. Davies⁷ examined VCM-P copolymerization where VCM was

TABLE I
Equilibrium Pressure of Comonomer Mixture

Composition in reactor			Equilibrium pressure at 50°C, psi
Vinyl chloride	Propylene	Polymer ^a	
384	16	0	123
376	24	0	128
368	32	0	134
360	40	0	137
352	48	0	141
344	56	0	147
229	37	133	147
116	18	266	146
336	64	0	152
328	72	0	156
320	80	0	161
312	88	0	166

^a Preformed VCM-P copolymer of 2.7% bound propylene.

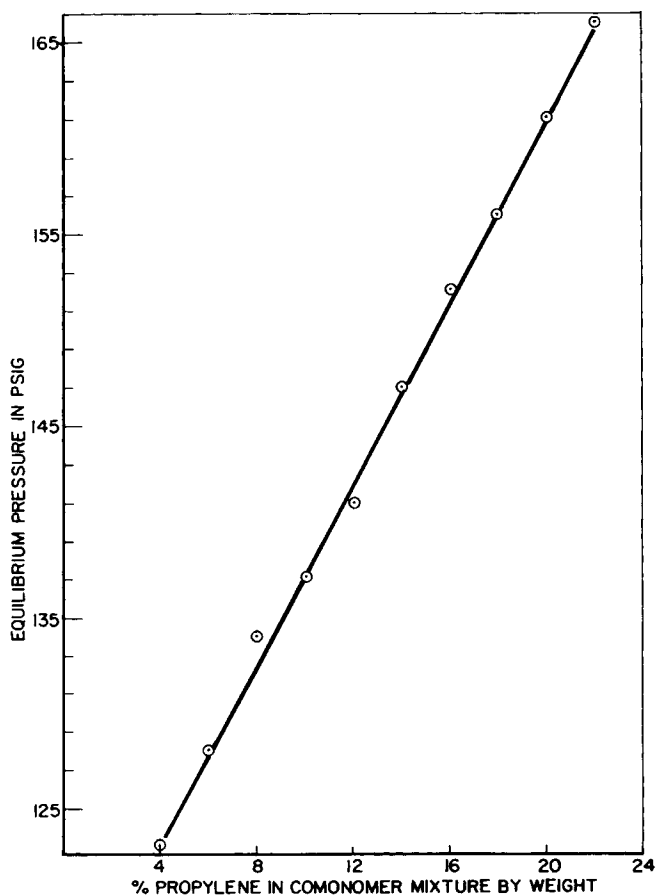


Fig. 1. Equilibrium pressure of mixtures of VCM-P comonomer in simulated polymerization systems at 50°C.

TABLE II
Physical Properties of VCM/P Copolymers Prepared at Constant Equilibrium Pressure

Temp. of poly- meriza- tion, °C	Ratio VCM/P charged	Equi- librium pressure, psig	Con- version, %	Inherent viscosity	Melt flow, g/10 min	% Pro- pylene bound
50	95/5	128	74.0	.767	2.20	2.54
50	91/9	135	69.7	.678	11.8	3.80
50	90/10	138	61.3	.623	27.0	4.37
50	82/11	141	26.3	.627	30.0	—
50	89/11	141	42.3	.635	34.0	—
50	89/11	141	67.1	.630	32.5	4.48
50	87/13	146	55.7	.553	136	5.28
50	85/15	149.5	47.0	.513	210	6.15

fed into a reactor in a manner in which the equilibrium vapor pressure was controlled by intermittent addition of vinyl chloride monomer.

In order to use equilibrium pressure (P_{eq}) of the unreacted comonomer as a control parameter, a linear relationship between propylene content in the monomer ($\%P_c$) and equilibrium pressure needed to be established. In addition, the effect of copolymer in the unreacted comonomer mixture must be such that there is no effect on P_{eq} . The P_{eq} values of comonomer mixtures were determined by a procedure detailed in the experimental section. The results are detailed in Table I. This is graphically represented in Figure 1.

A series of VCM-P copolymers of uniform composition were prepared by a procedure detailed in the experimental section. The P_{eq} , as noted in Table II, for each of the individual runs was maintained at a fixed level by means of manual venting. In this manner, a uniform composition copolymer would be formed. The MF and IV properties of these copolymers are also noted in Table II.

Batch copolymers of VCM-P were prepared by a procedure detailed in the experimental section. The heat of polymerization output of the polymerization was determined in a continuous manner. As a result, cumulative per cent conversion at any time was known. The data are noted in Table III. Samples of resin were removed from the reactor at various times, and MF and IV properties were determined at different conversion levels. These properties are noted in Table IV. In this study, the heat of polymerization used for vinyl chloride was 91.7 Btu/gram-mole.

EXPERIMENTAL

Material

Water: tap water passed through a deionization column and then distilled under a nitrogen purge.

Suspending agent: Methocel K-35, from Dow Chemical, used as received.

Initiator: *t*-butyl perneodecanoate; 75% active in odorless mineral spirits, from U.S. Peroxygen, used as received.

Monomers: propylene obtained from Air Products Specialty Gas Division, C.P. grade, used as received.

TABLE III
Instantaneous Output Data and Cumulative Conversion
For VCM/P Copolymer^a

Time, min	Copolymer A			Copolymer B		
	Btu (I)	Btu (C)	Con- version; (C), %	Btu (I)	Btu (C)	Con- version; (C), %
15	4.5	4.5	1.5	3.5	3.5	1.2
30	7	11.5	3.9	6.5	10	3.4
45	9.5	21	2.2	7.5	17.5	6.0
60	9.5	30.5	10.4	8.5	26	8.9
75	10	40.5	13.9	9	35	11.9
90	10	50.5	17.2	9.5	44.5	15.2
105	10.5	61	20.8	10	54.5	18.6
120	11	72	24.5	10	64.5	22.0
135	11	83	28.3	10	74.5	25.4
150	10.5	93.5	31.9	10	84.5	28.8
165	10	103.5	35.3	9.5	94	32.0
180	9.5	113	38.6	9	103	35.1
195	9	122	41.2	9	112	38.1
210	8.5	130.5	44.5	8.5	120.5	41.0
225	8.5	139	47.4	8	128.5	43.8
240	8	147	50.1	7.5	136	46.3
255	7.5	154.5	53.6	7	143	48.7
270	7	161.5	55.1	6.5	149.1	50.9
285	6.5	168	57.2	6	155.5	52.9
300	6	174	59.5	5.5	161	54.8
315	5.5	179.5	61.2	5.5	166.5	56.7
330	5	184.5	62.9	5	171.5	58.4
345	5	189.5	64.6	4.5	176	59.9
360	4.5	194	66.2	4	180	61.3
375	4	198	67.5	4	184	62.7
390	3.5	201.5	68.7	4	188	64.0
405	3.5	205	70.0	3.5	191.5	65.2
420	3	208	71.0	3	194.5	66.2
435	2.5	210.5	71.8	2.5	197	67.1
450	2.5	213	72.6	2	199	67.8
465	2	215	73.4	2	201	68.4
480	1.5	216.5	73.9	1.5	207.5	69.0
495	1.5	278	74.4	1.5	204	69.5
510	1	219	74.7	1	205	69.8
525	1	220	75.0	1	206	70.1
540	1	221	75.3	1	207	70.4
555				.5	207.5	70.7
570				.5	208	70.8
585				.5	208.5	71.0
600				0	208.5	71.0
615				0	208.5	71.0
630				0	208.5	71.0

^a Btu(I) is average reading in Btu/min during each 15-min period. Btu(C) is cumulative Btu output from start of copolymerization. Conversion(C) is cumulative per cent conversion based on cumulative Btu output.

TABLE IV
Physical Properties of Type A and Type B Resin Versus Time^a

Time	Type A resin			Type B resin		
	Con- version, %	IV	MF	Con- version, %	IV	MF
1½	7.6	.683	—	15.2	.642	—
3	38.0	.719	3.0	35.1	.678	9.6
4½	54.9	.726	3.3	50.9	.682	9.4
6	65.9	.711	5.1	61.3	.675	14.8
7½	72.0	.708	6.6	67.8	.664	—
9	75.4	.701	7.4	70.4	.657	18.6
10½	—	—	—	71.0	.650	20.4
12	—	—	—	71.0	.646	22.0

^a Samples of resin withdrawn from reactor at indicated times; inherent viscosity and melt flow were then determined. Total slurry volume removed at each time was about 90 g in total.

Vinyl chloride obtained from Air Products Specialty Gas Division, C.P. grade, used as received.

Equipment Used For Equilibrium Pressure Studies and Synthesis of Composition Copolymers

Reactor: Type II reactor manufactured by Ingenieurbureau SFS, Zurich, Switzerland.

Temperature control: held to $\pm 0.2^\circ\text{C}$.

Pressure recording: Heise CMM 0-200 psi gauge calibrated at 100 psi to ± 0.5 psi using a dead weight tester, manufactured by Heise Gauge Company, Newton, Connecticut.

Determination of Equilibrium Pressure for Comonomer Mixture

(1) Water, 800 g; (2) Methocel K-35, 0.288; (3) polymer; (4) vinyl chloride and (5) propylene, 400 g (total).

Items 1, 2, and 3 (when used) were added to the reactor. The monomers, items 4 and 5, were then added and the reactor was heated to 50°C with vigorous stirring. Pressure readings were taken after isothermal conditions were achieved. Usually, 15 min were sufficient to obtain a four-pressure reading within ± 0.5 psi of each other.

Polymerization Procedure for Preparation of Uniform Composition Copolymers

(1) Water, 800 g (total); (2) Methocel K-35, 0.288 g; (3) *t*-butyl perneodecanoate, 2.0 ml; (4) vinyl chloride/propylene, 400 g (total); ratio of VCM-P varied to achieve different compositions.

Items 1, 2, and 3 were added consecutively to the reactor under a nitrogen purge system. The monomers were then added to the reactor and the temperature

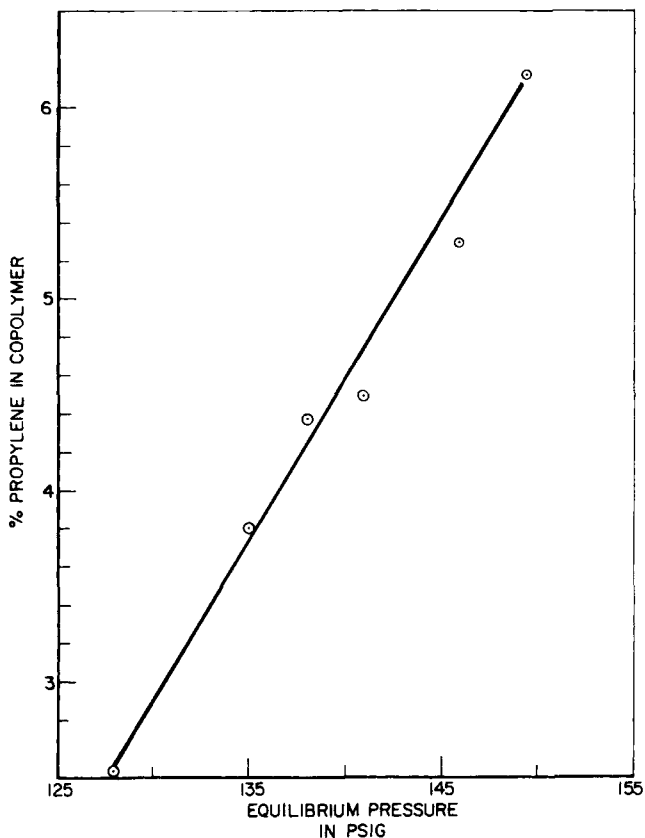


Fig. 2. Propylene content in copolymer ($\%P_B$) prepared at constant equilibrium pressure (P_{eq}).

was quickly raised to polymerization temperature. The polymerization was carried out for 8 hr. Polymerization was maintained at $50^\circ \pm 0.2^\circ\text{C}$. Pressure within the reactor was controlled within ± 0.5 psi of its initial value by cautiously venting the reactor head space.

Equipment Used for Batch Copolymers

Reactor: $3\frac{1}{2}$ gallon stainless steel pressure reactor. Temperature control for the slurry was maintained at $50^\circ \pm 0.2^\circ\text{C}$ during the polymerization. The total heat output of the polymerization was recorded to determine the conversion versus time.

Polymerization Procedure⁸ for Batch Copolymerization

(1) Water, 6000 g; (2) Methocel K-35, 2.16 g; (3) *t*-butyl perneodecanoate, 12 ml; (4) vinyl chloride and (5) propylene, 3000 g (total).

Ratio of VCM/P was varied to achieve different levels of propylene. Components were added in sequence. Components 1, 2, and 3 were added at once and the mixture was stirred. Component 4 was added followed by component

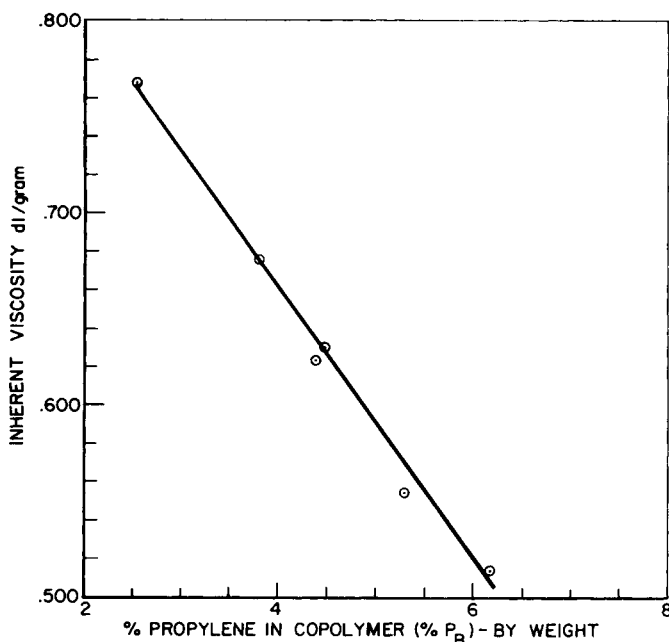


Fig. 3. Inherent viscosity of copolymers as a function of propylene content of polymer ($\%P_B$). Copolymers prepared at 50°C by constant equilibrium pressure (P_{eq}).

5. The mixture was stirred and heated to 50°C. The percentage of charged propylene in the two systems was: A, 7.0% propylene in the initial comonomer feed; B, 8.33% propylene in the initial comonomer feed. Polymerization was terminated when exothermic heat of polymerization fell to <1 Btu/min.

Resin slurry, 100 g, was withdrawn from the reactor each 1½ hr for testing purposes.

Polymer Test Procedures

Inherent viscosity (IV), ASTM Method D-1243-60-A; melt flow (MF), ASTM Method D-1238-57-T-Condition F. % propylene bound ($\%P_B$), by density using $ZnCl_2$ solution⁹ in a density gradient column. The values for density of propylene and vinyl chloride portions of the polymer were based on work of Ravey.¹⁰

RESULTS AND DISCUSSION

Equilibrium Pressure (P_{eq}) Versus % Propylene in the Reaction Mixture. A simulated polymerization recipe was prepared adding all of the components except initiator. This mixture was stirred and heated to polymerization temperature (50°C). After 15 min on temperature, P_{eq} was recorded. These results are noted in Table I and Figure 1. In certain cases a constant VCM/P ratio was maintained and a preformed copolymer of VCM/P was introduced into the mixture. The purpose was to determine if a copolymer would affect the P_{eq} of the unreacted comonomer mixtures. There was no change in P_{eq} at two levels of polymer. Based on these results, it was assumed that changes in the comono-

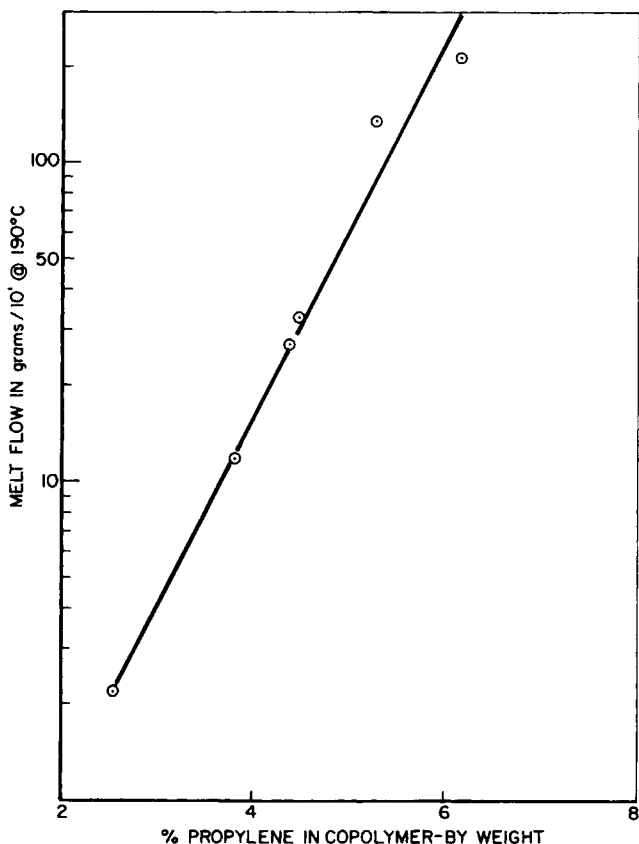


Fig. 4. Melt flow of copolymers as a function of propylene content of the polymer ($\%P_B$). Copolymers prepared at 50°C by constant equilibrium pressure (P_{eq}).

nomer ratio will affect P_{eq} in a linear fashion and that the presence of polymer, up to 67%, would not affect P_{eq} .

Equilibrium Pressure Versus % Propylene Bound in Copolymer. A series of VCM/P copolymers were prepared at 50°C and at different ratios of VCM/P. Melt flow, IV, and bound % propylene properties of these resultant copolymers are detailed in Table II. A plot of data of equilibrium pressure versus % propylene bound in copolymer (Fig. 2) indicates that there is a linear relationship between these two parameters.

Extent of Polymerization Versus Melt Flow and Inherent Viscosity Properties of Copolymer. Effects of extent of conversion on copolymer properties were studied. In Table II, runs 4, 5, 6, and 7 indicated that over a range of conversion of 26% to 67%, properties of IV and MF did not change. This was an additional indication that by maintaining a constant P_{eq} , copolymer composition would not vary during conversion.

Inherent Viscosity Versus % Propylene Bound in the Copolymer. A plot of the data of IV and $\%P_B$ from Table II indicated a linear relationship for these two variables. This is noted in Figure 3.

Melt Flow Versus % Propylene Bound in the Copolymer. It was found that there is an empirical relationship between melt flow properties of a resin

TABLE V
Computer Printout of Instantaneous Composition of Polymer A Formed at each
1% Conversion Increment. Based on an Initial Comonomer Ratio of
VCM/P of 93/7 and R_1/R_2 of 2.90/0.0

INSTANTANEOUS CO POLYMER COMPOSITION OF A BINARY SYSTEM					
CON			CON		
%	W1%	W2%	%	W1%	W2%
1	97.56	2.43	2	97.54	2.45
3	97.52	2.47	4	97.51	2.48
5	97.49	2.50	6	97.47	2.52
7	97.46	2.53	8	97.44	2.55
9	97.42	2.57	10	97.40	2.59
11	97.38	2.61	12	97.36	2.63
13	97.34	2.65	14	97.32	2.67
15	97.30	2.69	16	97.28	2.71
17	97.26	2.73	18	97.24	2.75
19	97.22	2.77	20	97.19	2.80
21	97.17	2.82	22	97.15	2.84
23	97.12	2.87	24	97.10	2.89
25	97.07	2.92	26	97.05	2.94
27	97.02	2.97	28	96.99	3.00
29	96.97	3.02	30	96.94	3.05
31	96.91	3.08	32	96.88	3.11
33	96.85	3.14	34	96.82	3.17
35	96.79	3.20	36	96.75	3.24
37	96.72	3.27	38	96.69	3.30
39	96.65	3.34	40	96.62	3.37
41	96.58	3.41	42	96.54	3.45
43	96.50	3.49	44	96.46	3.53
45	96.42	3.57	46	96.38	3.61
47	96.33	3.66	48	96.29	3.70
49	96.24	3.75	50	96.19	3.80
51	96.14	3.85	52	96.09	3.90
53	96.03	3.96	54	95.98	4.01
55	95.92	4.07	56	95.86	4.13
57	95.80	4.19	58	95.74	4.25
59	95.67	4.32	60	95.60	4.39
61	95.53	4.46	62	95.45	4.54
63	95.37	4.62	64	95.29	4.70
65	95.20	4.79	66	95.11	4.88
67	95.02	4.97	68	94.92	5.07
69	94.81	5.18	70	94.70	5.29
71	94.58	5.41	72	94.46	5.53
73	94.33	5.66	74	94.19	5.80
75	94.04	5.95	76	93.88	6.11
77	93.72	6.27	78	93.53	6.46
79	93.34	6.65	80	93.13	6.86

MEAN VALUE OF W1 = 96.24 W2 = 3.75

and level of bound % propylene in resin. In Figure 4 are the data for log of MF versus % P_B for the resins prepared at 50°C. Melt flow properties were determined in a Tinus-Olsen melt tester according to ASTM test procedure D-1238-57-T (condition F).

Prediction of Variation in Bound Propylene Level as a Function of Conversion. A computer program was developed using a Wang 720C computer,

TABLE VI
 Computer Printout of Instantaneous Composition of Copolymer B Formed at Each
 1% Conversion Increment. Based on an Initial Comonomer Ratio of VCM/P
 of 91.67/8.33 and R_1/R_2 of 2.90/0

INSTANTANEOUS CO POLYMER COMPOSITION OF A BINARY SYSTEM					
CON			CON		
%	W1%	W2%	%	W1%	W2%
1	97.09	2.90	2	97.07	2.92
3	97.05	2.94	4	97.03	2.96
5	97.01	2.98	6	96.99	3.00
7	96.97	3.02	8	96.95	3.04
9	96.92	3.07	10	96.90	3.09
11	96.88	3.11	12	96.86	3.13
13	96.83	3.16	14	96.81	3.18
15	96.78	3.21	16	96.76	3.23
17	96.73	3.26	18	96.71	3.28
19	96.68	3.31	20	96.65	3.34
21	96.63	3.36	22	96.60	3.39
23	96.57	3.42	24	96.54	3.45
25	96.51	3.48	26	96.48	3.51
27	96.45	3.54	28	96.42	3.57
29	96.38	3.61	30	96.35	3.64
31	96.32	3.67	32	96.28	3.71
33	96.24	3.75	34	96.21	3.78
35	96.17	3.82	36	96.13	3.86
37	96.09	3.90	38	96.05	3.94
39	96.01	3.98	40	95.96	4.03
41	95.92	4.07	42	95.87	4.12
43	95.83	4.16	44	95.78	4.21
45	95.73	4.26	46	95.68	4.31
47	95.63	4.36	48	95.57	4.42
49	95.51	4.48	50	95.46	4.53
51	95.40	4.59	52	95.33	4.66
53	95.27	4.72	54	95.20	4.79
55	95.14	4.85	56	95.06	4.93
57	94.99	5.00	58	94.91	5.08
59	94.83	5.16	60	94.75	5.24
61	94.66	5.33	62	94.57	5.42
63	94.48	5.51	64	94.38	5.61
65	94.28	5.71	66	94.17	5.82
67	94.05	5.94	68	93.93	6.06
69	93.81	6.18	70	93.68	6.31
71	93.54	6.45	72	93.39	6.60
73	93.23	6.76	74	93.07	6.92
75	92.89	7.10	76	92.70	7.29
77	92.50	7.49	78	92.28	7.71
79	92.05	7.94	80	91.80	8.19

MEAN VALUE OF W1 = 95.52 W2 = 4.47

which printed out the instantaneous copolymer composition of a binary comonomer system as a function of conversion. Printouts for system A based on a comonomer ratio of VCM/P = 93/7 and system B based on a comonomer ratio of VCM/P = 91.67/8.33 are tabulated in Tables V and VI. Reactivity ratios of $R_1(\text{VCM}) = 2.90$ and $R_2(\text{P}) = 0$ were used for these calculations.¹¹

TABLE VII
Cumulative Properties of A Type Resin^a

Con- version, %	% $P_B(I)$	IV(I)	IV(C)	MF(I)	MF(C)
5	2.50	.770	.770	2.10	2.10
10	2.59	.762	.767	2.30	2.20
15	2.69	.755	.762	2.65	2.34
20	2.80	.747	.758	3.10	2.51
25	2.92	.738	.754	3.70	2.71
30	3.05	.730	.750	4.40	2.94
35	3.20	.720	.746	5.20	3.19
40	3.37	.705	.740	6.80	3.51
45	3.57	.691	.735	9.00	3.89
50	3.80	.675	.729	12.3	4.37
55	4.07	.655	.723	17.8	4.97
60	4.39	.631	.715	27.5	5.71
65	4.79	.602	.706	47.0	6.73
70	5.29	.540	.694	94.0	8.11
75	5.95	.517	.682	235	10.15

^a % $P(I)$ is instantaneous propylene composition of copolymer formed at indicated conversion. Data taken from Table V. IV(I) is predicted IV of the instantaneous copolymer formed at indicated conversion. Data developed from Figure 3. IV(C) is predicted IV of the cumulative copolymer formed at indicated conversion. Data are developed by arithmetic summation of IV(I) terms. MF(I) is the predicted MF of instantaneous copolymer formed at indicated conversion. Data developed from Figure 4. MF(C) is predicted MF of cumulative copolymer formed at indicated conversion. Data are developed by arithmetic summation of log MF(I) terms.

Prediction of Variation in Melt Flow and Inherent Viscosity Properties as a Function of Bound Level of Propylene. Data in Tables V and VI predict, for these batch copolymerization of VCM/P, how instantaneous polymer composition will change with conversion, using reactivity ratios defined above. The bound level of propylene (% P_B) at each 5% increment was tabulated in Table VII for a 93/7 copolymer system and in Table VIII for a 91.67/8.33 copolymer system. Predictions could now be made as to what MF and IV values should be for a batch-copolymerized VCM-P system. The % P_B in each 5% increment could be used to correlate MF and IV contribution of that increment to the total polymer properties. These data are tabulated in the column "Instantaneous IV" and "Instantaneous MF." The cumulative values for IV and MF, as a function of conversion, were determined by a summation of each term. Cumulative inherent viscosity was an arithmetic summation; cumulative melt flow was determined by an arithmetic summation of log values of MF.¹²

Comparison of Predicted Versus Experimental Properties as a Function of Conversion

Melt Flow Properties. In Figure 5, we have plotted the predicted values for MF versus conversion based on the data from Tables VII and VIII. The experimental values for MF for the two copolymer systems are also plotted in Figure 5. The data indicate a close agreement between the predicted values of MF and the experimental values.

TABLE VIII
Cumulative Properties of Type B Resin^a

Con- version, %	%P _B (I)	IV(I)	IV(C)	MF(I)	MF(C)
5	2.98	.735	.735	4.0	4.00
10	3.09	.727	.731	4.6	4.30
15	3.21	.717	.726	5.5	4.66
20	3.34	.707	.721	6.6	5.08
25	3.48	.697	.717	7.9	5.56
30	3.64	.687	.712	10.0	6.12
35	3.82	.675	.706	12.5	6.70
40	4.03	.657	.700	17.0	7.60
45	4.26	.642	.694	26	8.73
50	4.53	.622	.687	34	9.98
55	4.85	.597	.678	52	11.6
60	5.24	.570	.669	90	13.7
65	5.71	.535	.659	180	16.8
70	6.31	.491	.647	380	20.9
75	7.10	—	—	—	—

^a %P(I) is instantaneous propylene composition of copolymer formed at indicated conversion. Data taken from Table VI. IV(I) is predicted IV of the instantaneous copolymer formed at indicated conversion. Data developed from Figure 3. IV(C) is predicted IV of the cumulative copolymer formed at indicated conversion. Data are developed by arithmetic summation of IV(I) terms. MF(I) is the predicted MF of instantaneous copolymer formed at indicated conversion. Data developed from Figure 4. MF(C) is predicted MF of cumulative copolymer formed at indicated conversion. Data are developed by arithmetic summation of log MF(I) terms.

Inherent Viscosity Properties. In Figure 6, predicted values of IV are plotted versus conversion. The experiment values for these two copolymers are also plotted in Figure 6. The predicted cumulative IV decreases with conversion in a continuous manner. Experimental data exhibit a cumulative IV which rises to a maximum value at about 50% conversion and then decreases between 50% and 70% conversion. The experimental data of cumulative IV versus conversion can be interpreted to be two competing reactions: (1) an initial reaction in the period from 0% to 45% in which molecular weight is increasing to a maximum value of IV; and (2) a second reaction in the period from 45% to 75% in which molecular weight decreases. The phenomenon of increased IV with conversion in the range of 0–45% has been noted by Cotman et al.¹³ in their study of vinyl chloride polymerization. They interpreted this as due to immobilization of the

TABLE IX
Homopolymer IV Versus Conversion^a

Conversion, %	IV
7.2	.735
18.5	.815
60	.865
75	.875
86	.882

^a Polymerized at 56°C. Conditions of polymerization: VCM, 100 parts; H₂O, 200 parts; Methocel K-35, 0.07 parts; *t*-butyl perneodecanoate, 0.05 parts.

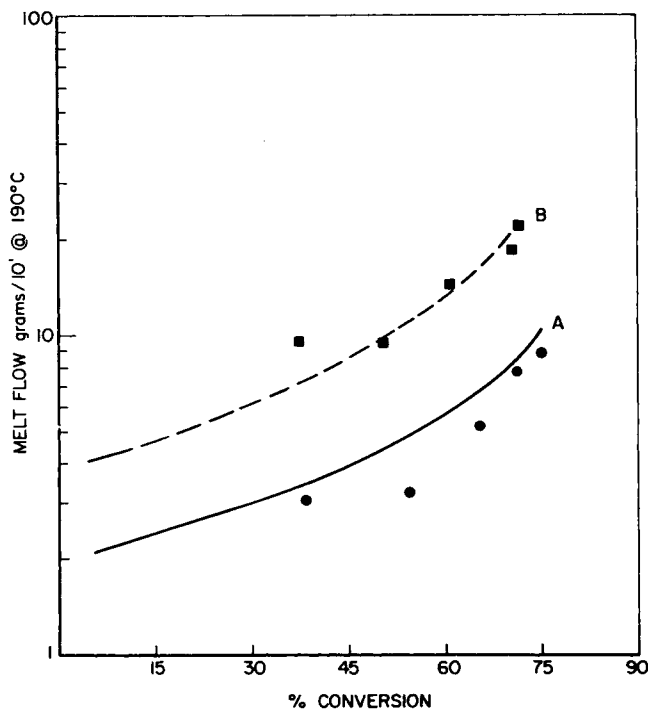


Fig. 5. Melt flow of batch-copolymerized VCM-P as a function of conversion. Resin A: 7% propylene in initial comonomer feed; (●) experimental points; (—A) calculated line. Resin B: 8.33% propylene in initial comonomer feed; (■) experimental points; (- - - B) calculated line.

polymer radical within the solid and a corresponding decrease in mutual chain termination. Cotman's observation was confirmed in this paper during the preparation of the homopolymer of VCM using *t*-butyl perneodecanoate initiator. The inherent viscosity of the homopolymer was determined as a function of conversion. These data are detailed in Table IX.

This study of the cumulative inherent viscosity of the batch copolymers of VCM/P took into consideration only effects of varying comonomer compositions on molecular weight of the copolymer being formed at any conversion. The effect described by Cotman¹³ was not considered. Decrease in cumulative IV from its maximum is interpreted as due to effects of the change in compositions of unreacted monomer. The initial composition for comonomer for type A resin was 7% propylene. At 50% conversion point, the propylene content of unreacted monomer was 11%. For the type B resin, initial propylene constant of comonomer was 8.33%. At 50% conversion, propylene content of unreacted monomer was 13%. At these high levels of propylene in unreacted comonomer, the predicted effect of decreased IV due to propylene becomes dominant over kinetic effects described by Cotman.

CONCLUSIONS

A. A uniform compositional copolymer can be prepared from a VCM-P system by a technique where equilibrium pressure in the vapor phase is maintained at a constant level.

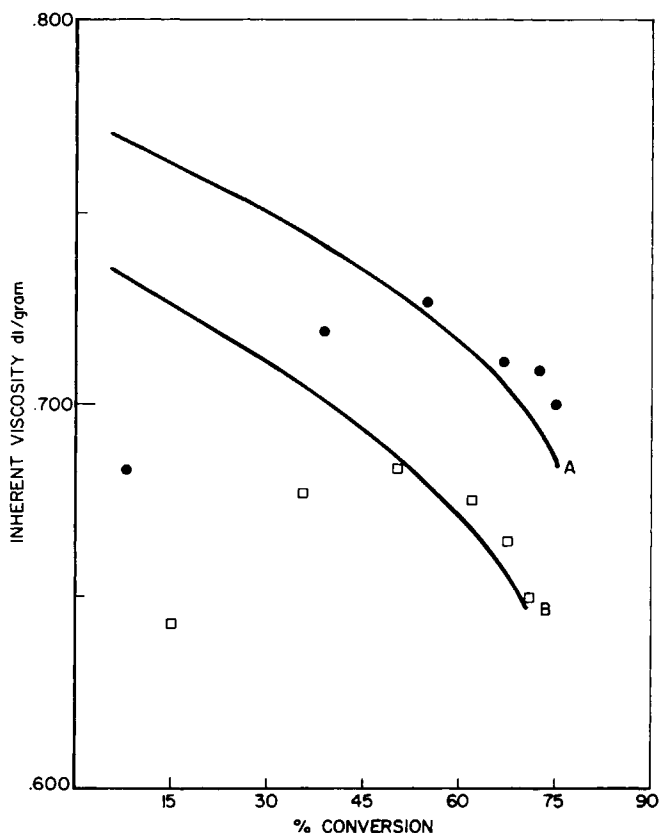


Fig. 6. Inherent viscosity of batch-copolymerized VCM-P as a function of conversion. Resin A: 7% propylene in initial comonomer feed; (●) experimental points; (—A) calculated line. Resin B: 8.33% propylene in initial comonomer feed; (□) experimental point; (—B) calculated line.

B. The properties of melt flow and inherent viscosity for these uniform composition copolymers were found to be related to the bound level of propylene in the resin.

C. Melt flow property for a batch polymerized VCM-P copolymer can be calculated knowing compositional variation in bound propylene at small increments of conversion and melt flow properties for each of these small increments.

D. Inherent viscosity properties for batch-polymerized VCM-P copolymers were found to be effected by two competing reactions. At low conversions (<50%), an increase in inherent viscosity was observed. At higher conversions (>50%), a second and more dominant reaction, probably caused by the relative high level of unreacted propylene in the comonomer system, caused the inherent viscosity to decrease with conversion.

Symbols

VCM vinyl chloride
P propylene

- P_{eq} equilibrium pressure
% P_B per cent propylene bound in copolymer
MF melt flow
IV inherent viscosity
(I) instantaneous
(C) cumulative

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