Kinetics of 1-Hexene Polymerization

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Synopsis

Kinetics of 1-hexene polymerization was studied by following the amount of unreacted monomer using gas chromatography. The Ziegler-Natta catalyst system used was comprised of $TiCl_4$-$AlEt_3$ with Al : Ti ratio of 0.85. The sampling and monomer analysis techniques developed can be applied to study the kinetics of higher α-olefins polymerizations, in general. Also, with minor modifications in this technique, a precise profile of molecular weight can be obtained during polymerization.

INTRODUCTION

Polymerization of 1-hexene using a variety of Ziegler-Natta catalysts was carried out to produce polymers having both different stereospecificities and molecular weights. The kinetics of 1-hexene polymerization, however, has been reported in only two instances. Badin[1] has polymerized 1-hexene to a low molecular weight liquid using the catalyst system $TiCl_4$-$Al(i-C_4H_9)_3$. The rate of polymerization was studied by subjecting the samples from reaction mixture to unsaturation analysis using titrimetric methods. Tu et al.[2] have conducted a systematic kinetic study of 1-hexene polymerization in cyclohexane with the catalyst system α-$TiCl_3$-$AlEt_2Cl$. The rate of polymerization was followed by analyzing the weight of the polymer obtained after the various time intervals. This implied that several reactions were carried out under identical conditions at varying lengths of time.

The use of gas chromatography (GC) in the investigation of copolymer reactivity ratios has been previously reported.[3-5] However, GC has not been a generally popular technique in studies involving either polymerizations or copolymerizations. In the present work, kinetics of 1-hexene polymerization in *n*-heptane with the catalyst system $TiCl_4$-$AlEt_3$ was studied by following the amount of unreacted monomer in the reaction mixture using GC. It has been shown that GC can be a valuable tool in following the polymerizations of higher α-olefins.

EXPERIMENTAL

Materials

$TiCl_4$, $AlEt_3$, and methanol were purchased from Aldrich Chemical Co. These chemicals were of highest available purity and were used without further purification. 1-Hexene was dried over molecular sieves and distilled prior to use. *n*-Heptane was dried over $CaCl_2$, distilled, and stored over sodium ribbon. $AlEt_3$ was procured as a 1.9 *M* solution in toluene and was

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TABLE I
Polymerization of 1-Hexene, Reaction Conditions and Polymer Molecular Weights

| Run no. | Monomer | | Catalyst wt% based on monomer wt | Initial reaction volume mL | Polymer yield g (2nd fraction) | % Discrepancy in mass balance | Intrinsic viscosity[a] 25°C | | $M_v \times 10^{-5}$ using relationship[b] $[\eta] = 2.32 \times 10^{-4}\ M^{0.69}$ THF |
	(mole)	Initial M Conc. mol/liter					Hexane	Tetrahydrofuran (THF)	
1	0.237	0.851	4	278.95	8.42 (0.8)	5.4	2.33	1.92	4.776
2	0.186	0.685	5	272.62	8.96 (0.5)	8.0	2.70	2.38	6.535
3	0.185	0.685	4	270.00	9.13 (0.51)	3.5	2.34	1.01	1.893
4[c]	0.185	0.685	1	270.00	3.24 (0.54)	—	0.62	0.39	0.4873

monomer–1-hexene   solvent—n-heptane

temp.—25°C, time–48 hr, catalyst–TiCl$_4$, AlEt$_3$ Al : Ti = 0.85

[a] Measured in Cannon-Ubelhode dilution viscometer.

[b] k and a values from Ref. 6.

[c] Reaction time was 30 hrs.

diluted to a desired concentration with toluene before use. The standard solutions of $TiCl_4$ were prepared in toluene. The catalysts and their solutions were handled under dry nitrogen atmosphere in a Labconco glove box. All glass equipment was thoroughly cleaned, dried overnight at 120°C, cooled, and stored under a nitrogen blanket before use.

Polymerization and Sampling Technique. All polymerizations were conducted at 25°C in Aldrich sure/seal bottles equipped with a magnetic stirrer. A typical polymerization procedure was as follows:

Purified n-heptane was placed in a 1 liter Aldrich sure/seal bottle. Dry nitrogen was flushed through the solvent for 30 mins. The solvent evaporation during nitrogen flush was found to be negligible as most of the bottle "top" was covered with paraffin film, and also the nitrogen was bubbled at a moderate rate. After the nitrogen flush, the bottle was capped with an Aldrich sure/seal, and catalyst solutions were introduced through the septum via gas tight syringes. The sequence of the addition of catalyst components was $AlEt_3$ followed by $TiCl_4$. The catalyst was allowed to digest for exactly 15 mins, at which point 1-hexene was introduced. Polymerizations were carried out for a period of 48 hours. Aliquots of 0.2 mL were removed at definite time intervals by means of a needle syringe. The damage to the septum due to several needle piercings was minimized by using special needles (Popper & Son, Inc., N.Y.) especially designed to work with septa. Each sample was poured onto 1 mL of methanol placed in a sample vial. The use of excess nonsolvent assured a complete precipitation of the polymer. The supernatants from each sample vial were subjected to GC analysis for unreacted 1-hexene. In the case of some samples, the small amount of polymer obtained on the precipitation with methanol was analyzed for intrinsic viscosity.

At the end of 48 hours, the reaction mixture was poured onto a large excess of methanol. The white rubbery polymer obtained was purified by dissolution in n-hexane and reprecipitation with methanol. The polymer was dried under

TABLE II
Conversion During First Hour

Run no.	t min	W $[M(m_0 - m)]$ g/liter	$[1 - m/m_0] \times 100$, %
1	20	1.22	1.70
	40	3.98	5.55
	60	4.72	6.59
2	20	1.35	2.34
	40	2.36	4.09
	60	3.11	5.40
3	30	0.74	0.43
	40	5.59	3.22
	50	6.84	3.95
4	30	3.26	5.64
	50	4.06	7.04
	60	4.13	7.16

Abbreviations: M = molecular weight of 1-hexene; m_0 = initial monomer concentration; m = monomer concentration at time t.

vacuum at ambient temperature to a constant weight. The low molecular weight ends were recovered by evaporation of the filtrate and were purified from hexane solution using methanol as the non-solvent.

Gas Chromatography (GC). The gas chromatograms of the samples were obtained with a Hewlet-Packard 5880A gas chromatograph equipped with a thermal conductivity detector and a $6' \times 1/8''$ SS column packed with 10% squalene on 100/120 mesh chromosorb WHP. The temperature profile of GC was: injector = 250°C; column = 1 min at 50°C followed by 20°C/min rise to 130°C, maintained at this temperature for 3 min, detector = 250°C.

TABLE III
Conversion and Intrinsic Viscosity as a Function of Time

Run no.	t hr	W g/liter	$[1 - (m/m_0)] \times 100$ %	$[\eta]$ dL/g hexane 25°C
1	0.66	3.84	5.37	
	5	13.20	18.45	2.92
	10	18.38	25.69	2.05
	20	24.64	34.44	2.49
	30	29.95	41.87	2.59
	45	36.42	50.91	2.74
	48	—	—	2.33
2	2.5	5.74	9.95	0.51
	3	6.66	11.55	0.69
	3.5	7.75	13.44	0.49
	4	9.36	16.23	0.53
	4.5	9.44	16.37	0.59
	18	22.31	38.69	1.46
	23	26.26	45.55	1.53
	28	29.38	50.96	1.87
	43	37.04	64.24	1.79
	48	39.06	67.74	2.34
3	1	3.24	5.62	—
	2	4.01	6.96	—
	3	5.56	9.64	2.34
	4	6.83	11.84	2.12
	5	10.85	18.81	4.25
	19	18.98	32.91	3.50
	24	24.79	42.97	4.10
	29	28.90	50.11	2.21
	43	31.51	54.64	4.02
	48	37.47	64.97	2.34
4	3	4.82	8.37	—
	4	5.70	9.90	0.56
	5	6.10	10.60	—
	10	8.51	14.79	—
	21	13.36	23.20	0.46
	26	14.78	25.67	1.31
	31	15.92	27.65	.83
	36	16.13	28.00	1.21
	45	17.60	30.57	0.58
	48	18.01	31.27	0.62

See Table II for abbreviation.

Since the samples analyzed constituted a mixture of 1-hexene, n-heptane, toluene, and methanol, a known mixture of these components was used as a calibration standard. A multilevel calibration was not needed since deviations in the response factor $\left(\dfrac{\text{calibration amount}}{\text{calibration area}}\right)$ for 1-hexene were very minor over a range of 3–15 vol%. The normalized volumes for 1-hexene, toluene, and heptane were derived from the respective peak areas. Methanol was left out of these calculations. The total unreacted 1-hexene in the reaction mixture was calculated using normalized volumes and the volume of the total reaction mixture.

The accuracy of GC analysis under simulated sampling conditions was tested by (i) preparing two mixtures similar to the calibration standard as described above, but varying in 1-hexene concentrations to reflect the conversions of < 5% and > 65%, (ii) adding different amounts of solid poly-1-hexene to these mixtures, and (iii) analyzing for 1-hexene, toluene, and heptane in the supernatants of these mixtures. The error in the GC analysis for 1-hexene monomer in the above mixtures was 1% and 2.5%, the highest being observed in the mixture with less monomer and more polymer. This indicates that calibration with a single standard would not be sufficient if kinetics is followed beyond 65% conversion. A multilevel calibration, however, would remedy this situation. The repeatability of the analysis was within 1%.
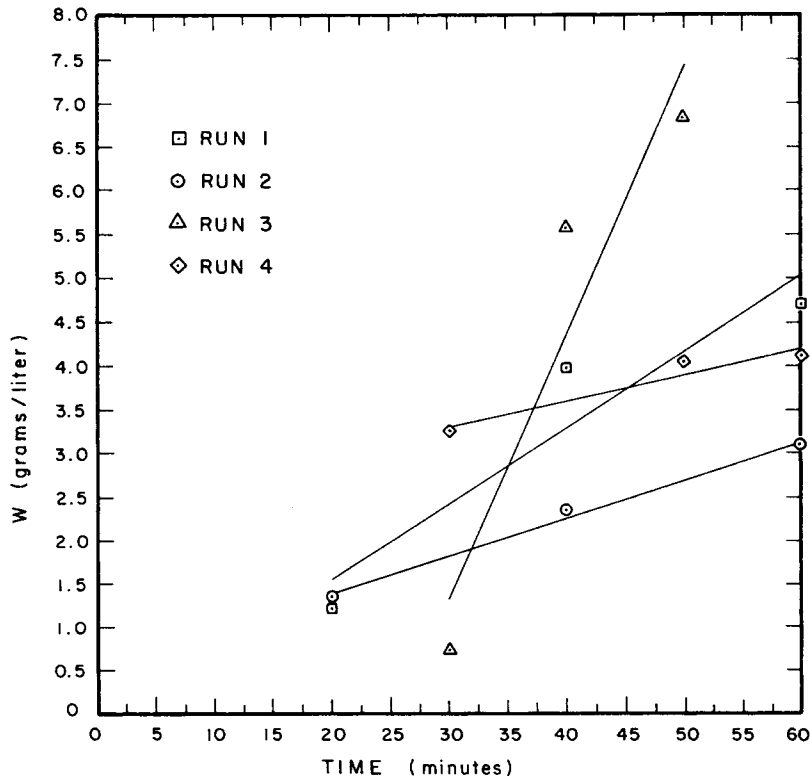

Fig. 1.   Dependence of weight concentration of polymer on time during first hour.

Gel Permeation Chromatography (GPC). A Waters' liquid chromatograph model 264 with a differential refractometer detector was used to obtain the molecular weight distribution (MWD) in polymers. Lichrogel PS40 and PS1 (E. Merck, Darmstadt, FRG) columns were used in series with tetrahydrofuran (THF) as the mobile phase. The flow rate was maintained at 1 mL/min, and a 50 μL polymer solution was injected following filtration through a 0.5 μm filter. The chart recorder speed was 0.5 cm/min.

RESULTS AND DISCUSSION

Table I summarizes the reaction conditions and results obtained for four 1-hexene polymerizations which were followed by GC. The effect of catalyst concentration and initial monomer concentration on the rate of polymerization, polymer yield, and molecular weight was studied. The actual quantity of monomer used in each polymerization is also given in Table I to show mass balance data. Since GC provided an accurate analysis of monomer under simulated sampling conditions, the discrepancy in mass balance was ascribed to the loss of low molecular weight ends during reaction work-ups.

The data in Table I indicate that a change in initial monomer concentration from 0.851 mol/liter to 0.685 mol/liter had no effect on the polymer yield at
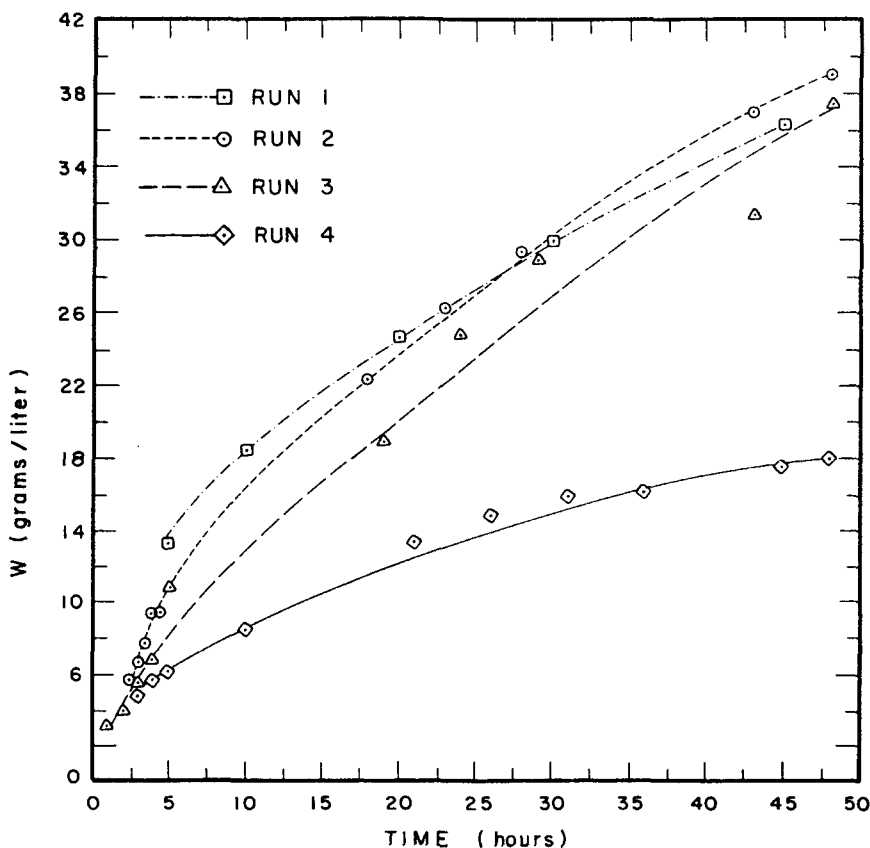

Fig. 2. Dependence of weight concentration of polymer on time.

the end of 48 hours. A decrease in catalyst concentration from 4 to 1%, however, decreased the polymer yield considerably. At a fixed time, intrinsic viscosity of the polymer increased with catalyst concentration, a phenomenon opposite to that observed in case of radical polymerization where higher catalyst concentrations usually result in lower molecular weight polymers.

The data obtained on the rates of polymerization are shown in Tables II and III. The format, in which these data are presented and plotted in Figures 1 and 2, was especially chosen to allow some comparison between reactivities of the systems α-TiCl$_3$-AlEt$_2$Cl and TiCl$_4$-AlEt$_3$. A direct comparison between these two systems was not possible since initial molar concentrations of monomer and catalyst components used in this work and by Tu et al.[2] were significantly different. For example, Tu et al.[2] used monomer: Al ratios ranging from 3 to 12.5 and monomer: Ti ratio from 12 to 50, while in this study these ratios were in the range of 75–85 and 105–107, respectively. However, at any of the above monomer/catalyst ratios, Tu et al.[2] obtained high conversions (30–45%) during the first 60 mins, while according to Figure 1, we were hardly able to reach 8% conversion at first hour and 50–65% conversion at the end of 48 hours. Figures 1 and 2 are indicative of the low reactivity of TiCl$_4$-AlEt$_3$ catalyst system compared to that of α-TiCl$_3$-AlEt$_2$Cl
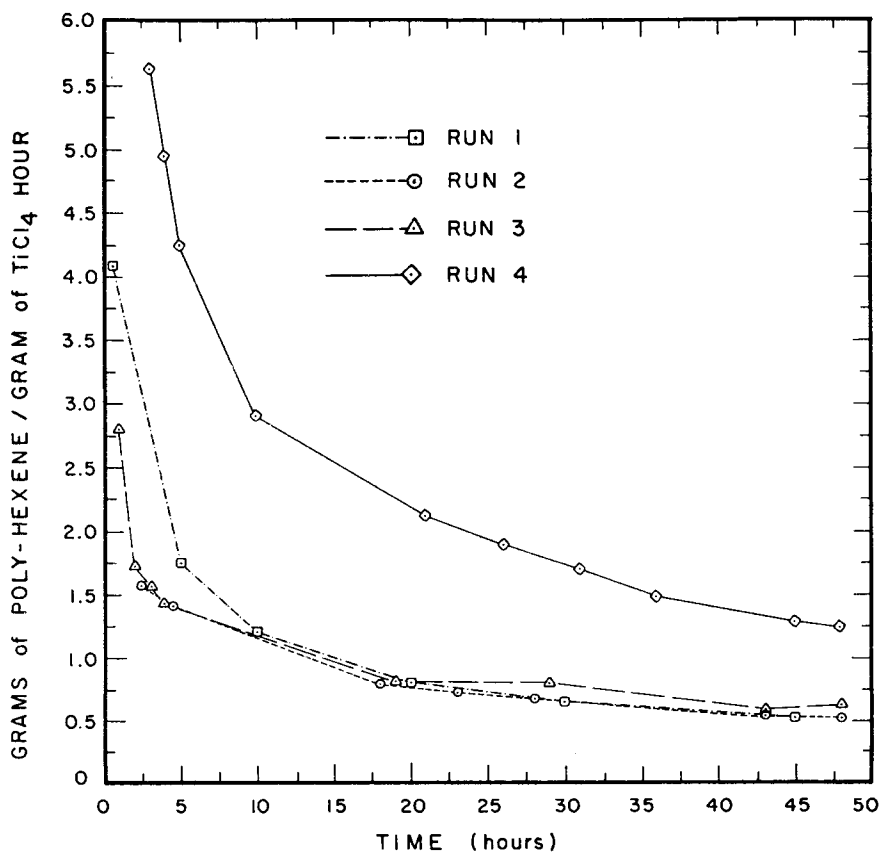

Fig. 3.   Poly-1-hexene kinetic curves (see Table I for reaction conditions).
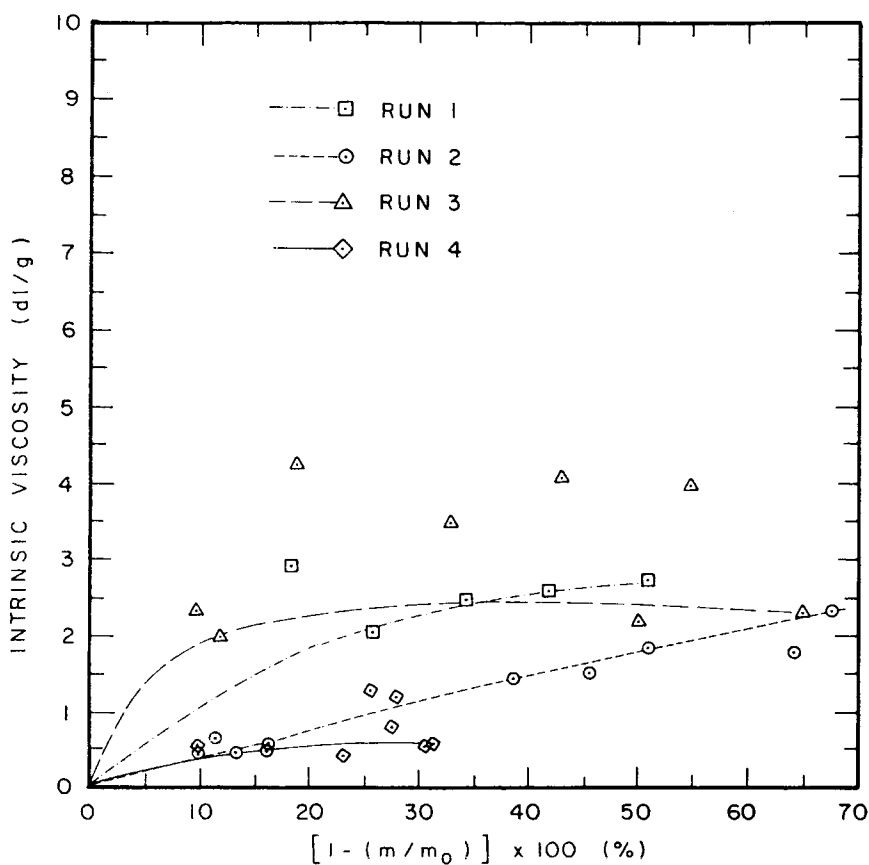
Fig. 4. Intrinsic viscosity as a function of conversion for poly-1-hexene from runs 1–4; 25°C, n-hexane.

TABLE IV

Polymerization of 1-Hexene, Reaction Conditions and Intrinsic Viscosities

monomer: 1-hexene	solvent: n-heptane
mole: 0.0594	catalyst: $TiCl_4$, $AlEt_3$
initial monomer	Al : Ti: 0.85
concentration: 0.851 mol/liter	catalyst concentration:
temperature: 25°C	4% based on monomer weight

Run no.	Time hr	Polymer yield %	Intrinsic viscosity $[\eta]$ dL/g 25°C, n-hexane
5	1	14.7	4.39
6	7	22.5	3.28
7	35	61.7	4.22
8	48	90.9	4.48

system studied by Tu et al.[2] The customary kinetic curves for 1-hexene polymerizations are shown in Figure 3.

High molecular weight polymers were obtained in the present work using Al : Ti ratio of 0.85. The viscosity average molecular weights of unfractionated polymers ranged from 48,000 to 650,000. An attempt was made to study the intrinsic viscosity profile of the polymer during the reaction. The results obtained are given in Figure 4, which shows a plot of intrinsic viscosity $[\eta]$ vs. conversion. The intrinsic viscosity of the polymers appears, in general, to remain constant once it has reached a certain maximum. The scatter observed in the values of intrinsic viscosity in some cases was probably due to the errors introduced solely by the very small quantity of polymer samples used. As only 0.2 mL was withdrawn from the reaction mixture for each sample to keep the changes in total volume negligible, less than 15 mg of polymer per sample was available for viscosity measurements. This translated into the viscosity measurements on extremely dilute solutions. The fact that the source of erratic data points in Figure 4 was the small quantity of sample, was confirmed by running 4 additional 1-hexene polymerizations shown in Table IV. The intrinsic viscosities of polymers obtained from these reactions at various lengths of
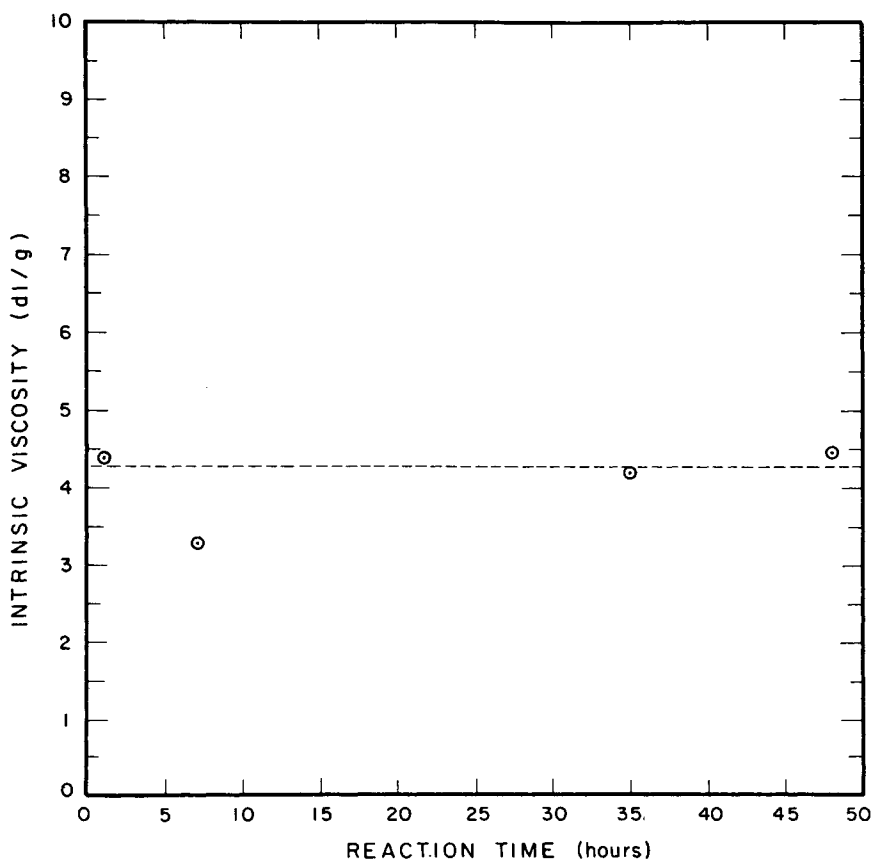

Fig. 5.   Intrinsic viscosity as a function of time for poly-1-hexenes from runs 5–8; 25°C, n-hexane.

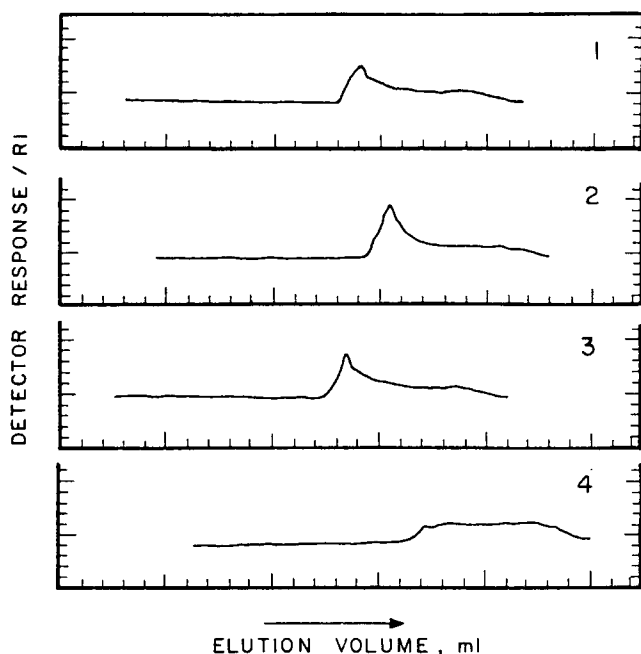DANDGE, HELLER, LIEN, AND WILSON

ELUTION   VOLUME , ml

Fig. 6.   GPC chromatograms of poly-1-hexene samples (from runs 1–4) in tetrahydrofuran at 25°C; sample size −0.2 mL; concentration 0.25 wt%; each division on x-axis corresponds to 1 mL; chromatograms begin at injection point.

time are plotted in Figure 5. The data indicate that the intrinsic viscosity, and hence the average molecular weight, remains almost constant throughout the course of the polymerization, although the magnitude of intrinsic viscosity was much higher compared to the values obtained for the runs which were followed by GC. This difference in the magnitude of viscosity may be due to the scaling-down of polymerizations reported in Table IV. The above observations indicate that while the rate of polymerization can be monitored by GC, it would be necessary to withdraw large enough samples if a more precise profile of polymer molecular weight during the reaction were to be observed.

The GPC chromatograms, represented in real scales and showing molecular weight distribution in polymers from runs 1–4, are given in Figure 6. It appears that the system $TiCl_4$-$AlEt_3$, under the experimental conditions used here, produces polymers with a broad molecular weight distribution. This is in contrast to the α-$TiCl_3$-$AlEt_2Cl$ system[2] where low molecular weight ends were not obtained. Also, Figure 6 clearly shows the difference in MWD of polymer obtained using 4% (or 5%) and 1% catalyst concentration. The latter does not show the presence of high molecular weight ends while the former has a distinct peak indicating the presence of large amount of high molecular weight polymer.

In conclusion, the kinetics of 1-hexene polymerization was studied using the catalyst system $TiCl_4$-$AlEt_3$ at Al/Ti ratio of 0.85. It was shown that GC can be used to follow the reaction rates in higher α-olefin polymerization by analyzing unreacted monomer at various intervals of time. A technique has been described for sampling and analysis of the unreacted monomer. To obtain a precise molecular weight profile during polymerization, withdrawal of

large enough samples from the reaction mixture was found to be necessary. Use can be made of the techniques developed in the present study to monitor unreacted monomers in the co- and ter-polymerizations of higher α-olefins with Ziegler-Natta catalysts.

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