# Polymerization of Olefins through Heterogeneous Catalysis. I. Low Pressure Propylene Polymerization in Slurry with Ziegler–Natta Catalyst

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## Synopsis

Propylene was polymerized in slurry over a $TiCl_3 \cdot \frac{1}{3}AlCl_3$ (Stauffer Type AA) catalyst with Al—$Et_2Cl$ cocatalyst at 60 psig pressure both with and without $H_2$ present. The effects of polymerization temperature, catalyst poisons, and type of slurry liquid were investigated, with particular emphasis on the yield, tacticity, and MWD of the resulting polymer. The highest yields and isotactic content were obtained with decane–heptane mixtures as a slurry liquid, while slurry liquids in which polypropylene was most soluble gave the narrowest MWD.

## INTRODUCTION

The polymerization of olefins, such as ethylene, propylene, and other co-polymers, over heterogeneous catalysts, is an enormous and rapidly developing industry. New catalysts and new processes are announced frequently, and there is intensive research directed towards understanding the fundamentals of these processes. In spite of a quarter-century of research, there are still wide areas where depth of understanding is lacking. The fundamental questions include a mechanistic understanding of the influence of catalyst type, additives, and polymerization conditions on the properties of the polymer (e.g., tacticity, molecular weight distribution, density, etc.) as well as a sufficiently good understanding of the reactor variables (e.g., mixing, temperature distribution, fluidization, etc.) so that reliable scale-up is possible. This series of papers represents one attempt at adding understanding to this important area of polymerization.

One of the key questions in heterogeneous polymerization is the cause of the characteristically broad molecular weight distribution (MWD) found in these systems. A number of workers[1–12] consider that there is a spectrum of active sites on the solid surface, each with a different activity, while others[13–22] propose that diffusion limitations due to polymer encapsulation of the catalyst lead to the observed breadth of chain lengths. A recent paper[22] discusses the issue and provides simulations from a detailed catalyst particle model which suggest that diffusion limitations can explain at least part of the experimental broadening. One of the first goals of the present series of papers is to provide comprehensive experimental data coupled with mechanistic modelling so as to allow these var-

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ious hypotheses to be tested. This will be done by a detailed comparison of mechanistic models with regard to their ability to predict diagnostic experiments. Several previous workers (e.g., Refs. 23–31) have reported experimental work of a similar nature, but both the range of operating conditions and the properties measured were limited.

This first paper presents new experimental data for the polymerization of propylene, showing the influence of polymerization temperature, catalyst poisons, and type of slurry liquid on the observed polymer properties. Polymer tacticity and molecular weight distribution as well as polymerization yield are measured for each experimental run. Here the catalyst system is a commercially available Stauffer-AA Type 1.1 $TiCl_3 \cdot \frac{1}{3}AlCl_3$ catalyst with $Al$—$Et_2Cl$ cocatalyst. The polymerizations were carried out in a slurry at $\sim$60 psig. Later papers in this series will deal with higher pressures, other reactor configurations, other catalyst systems, and will attempt to provide a synthesis of these (and other results) into a coherent picture of heterogeneous olefin polymerization.

## EXPERIMENTAL DETAILS

### Polymerization

Polymerization was carried out in 500-mL reactor bottles with the experimental system shown in Figure 1. The materials are as noted in Table I. The standard (base case) experimental conditions were as follows:

| | |
|---|---|
| $TiCl_3 \cdot \frac{1}{3}AlCl_3$ | $1.5 \times 10^{-3}$ mol/L |
| $Al$—$Et_2Cl$ (DEAC) | $7.5 \times 10^{-3}$ mol/L |
| Slurry liquid | 200 mL $n$-heptane |
| Polymerization temperature | 70°C |
| Polymerization time | 5 h |
| Polymerization pressure | 60 psig |

When $H_2$ was used as a chain transfer agent, the reactor was charged with 4 psig $H_2$ for 15 min before the pressure was raised to 60 psig by the addition of propylene.
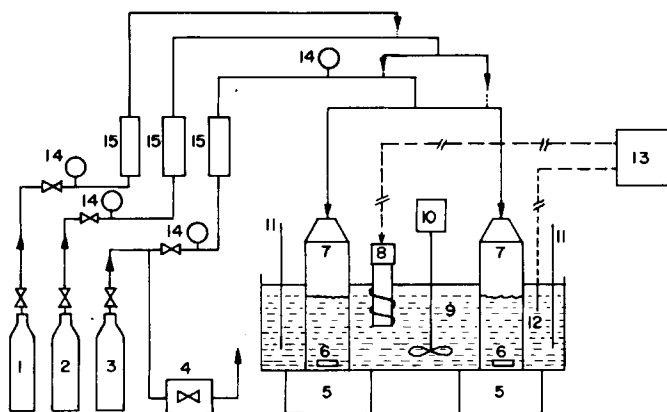


Fig. 1. Schematic of polymerization system: 1, $N_2$ cylinder; 2, $H_2$ cylinder: 3, $C_3H_6$ cylinder; 4, vent valve; 5, magnetic stirrer; 6, spin bar; 7, bottle reactor; 8, heater; 9, oil bath; 10, stirrer; 11, thermometer; 12, thermocouple; 13, temperature controller; 14, pressure gauge; 15, gas purification column.

TABLE I
Experimental Materials

| | |
|---|---|
| $TiCl_3 \cdot \frac{1}{3}AlCl_3$ | AA Type 1.1.  Commercial, Stauffer Chemical Company |
| $Al(C_2H_5)_2Cl$   (DEAC) | 15.1 wt % in heptane; Texas Alkyls Inc. (Cl/Al), mole ratio = 0.97 |
| n-Heptane | A.R., Mallinckrodt; the n-heptane is purified through washing, drying, and distillation |
| Propylene | Research grade, Matheson Co.; The propylene is purified by passing through molecular sieve 3A, Silica Gel. Ridox Columns |
| Nitrogen | Ultra High Purity, Matheson Co. |
| Hydrogen | Ultra High Purity, Matheson Co.; both are purified by passing through molecular sieve 4A, Silica Gel. Ridox Columns |
| Decane | 99 + %, Aldrich Chem. Co.; Decane is dried by metallic sodium for 7–10 days |
| Cyclohexane | A.C.S., Science Products Co.; Cyclohexane is purified as same as n-Heptane |
| Decalin | Spectro., Eastman Kodak Co. |
| Tetralin | Purified, Fisher Scientific Co.; tetralin is dried by metallic sodium for 7–10 days |
| Phenol | A.R., White Crystal, Scientific Products Co. |
| Isobutyl alcohol | A.R., Scientific Products Co. |
| 1,2,4-Trichlorobenzene (TCB) | 99+%, Aldrich Chem. Co. |
| Polystyrene standard | Waters Assoc. |
| Polypropylene standard | Polysciences Inc. |
| Trichloroacetic acid | A.C.S., Science Products Co. |

The reactor bottles were dried at 140–150°C for 4–5 h before being put into the glove box for catalyst addition.  The catalyst was handled in a glove box under very low $O_2$ and $H_2O$ levels (<5 ppm).  The $TiCl_3 \cdot \frac{1}{3}$ $AlCl_3$ catalyst was weighted into the reactor bottles and these were sealed with a drilled metal cap having a septum.  Purified and dried slurry liquid was added, and the bottles were placed into an oil bath under ±0.5°C temperature control.  After a temperature equilibration time of 1 h, the required amount of aluminum alkyl (DEAC) was injected by syringe and later other additives (if used) were injected.  Then the high purity $N_2$ was vented and the reactant gases, $H_2$ (if used) and propylene, were added until the total pressure was 60 psig.  This pressure was maintained constant by the addition of propylene throughout the polymerization.  Upon completion of the run, the bottles were degassed and injected with 5–10 mL of methanol containing HCl to deactivate the catalyst.  The violet color of the catalyst immediately changed to white.  The polymer was washed with methanol, filtered, dried, and weighed to determine polymer yield.  In each run, multiple reactor bottles were used to allow an estimate of the precision of the data.

## Tacticity Measurement

The tacticity of the polymer sample was obtained by extracting the purified polymer product with boiling heptane for 6 h using conventional Soxhlet extraction with cellulose thimbles.  The apparatus and procedure are similar to that described in Ref. 32.  The results are reported as percentage heptane insolubles, defined as

$$X_{HI} = \frac{\text{wt PP after extraction}}{\text{wt PP before extraction}} \times 100\%$$

and the reproducibility was determined from replicate runs in each case.

## Molecular Weight Measurement

The molecular weight distribution (MWD) of the polymer samples was determined through GPC analysis. The weighed polymer samples were dissolved in hot 1,2,4-trichlorobenzene (TCB), filtered through a 0.5-$\mu$ filter, and immediately analyzed using a Waters 150C GPC with twin Shodex A-80M/S columns. The GPC columns and injector were maintained at 143°C and the solvent flowrate was 0.8 mL/min. Preliminary runs were made at varying flow rates and sample holding times to insure that there was no thermal or mechanical degradation of the polymer during analysis. The GPC is connected to a computer data acquisition system which logs the data and provides a graphical and tabular report of the analysis.

Calibration of the columns for polypropylene was a problem due to the lack of availability of a broad range of narrow molecular weight polypropylene standards. The calibration used was a modification of a universal calibration procedure suggested by Westermann.[33] Narrow molecular weight polystyrene standards were used together with the Universal calibration concept to develop a polypropylene calibration curve. This curve was found to agree quite well with the reported molecular weights for two polypropylene standards which were available (cf. Fig. 2); further details may be found in Ref. 34.

## RESULTS AND DISCUSSION

### Effect of Polymerization Temperature

The first set of experimental runs was carried out to determine the influence of polymerization temperature on the rate of polymerization and the polymer properties. Four different temperatures (30, 50, 70, 90°C) were used both with and without $H_2$ addition. The results are tabulated in Table II and shown graphically in Figures 3–5. Note that both with and without $H_2$ addition the trends are the same and there is very little influence of $H_2$ addition except to reduce average molecular weight. This is in contrast to Okura et al.,[35] who found a rate increase with $H_2$ present while others[36–38] noted a sharp decrease in rate with $H_2$ addition. The measured polydispersity was only slightly higher with $H_2$ than without $H_2$.
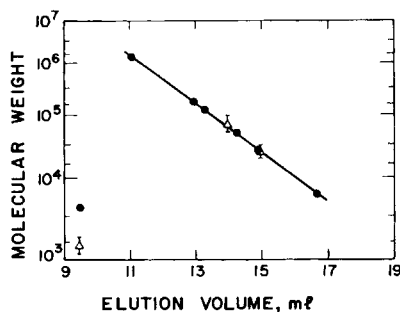


Fig. 2. GPC calibration curve. (●) Universal calibration standards.

TABLE II
Influence of Temperature on Polymer Yield and Properties

| Temp (°C) | $[M]_b$ (mol/L) | $[H_2]_b \times 10^3$ (mol/L) | $H_2$ added | Yield[a] (g PP/g Ti cat) | Average rate g PP/g Ti cat·h | Tacticity $X_{HI}$ (%) | $M_n \times 10^{-4}$ | $M_w \times 10^{-4}$ | $Q = M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 30 | 2.441 | 1.19 | yes | 134 | 26.8 | 95.7 ± 0.8 | 5.32 ± 0.14 | 37.5 ± 2.4 | 7.03 ± 0.27 |
|    |       |      | no  | 126 | 25.2 | 96.4 ± 0.5 | 8.10 ± 0.31 | 52.0 ± 0.8 | 6.41 ± 0.36 |
| 50 | 1.355 | 1.34 | yes | 255 | 50.9 | 97.8 ± 0.1 | 8.85 ± 0.43 | 57.5 ± 3.0 | 6.50 ± 0.03 |
|    |       |      | no  | 269 | 53.8 | 97.3 ± 0.1 | 11.46 ± 0.30 | 64.3 ± 1.9 | 5.62 ± 0.25 |
| 70 | 0.8076 | 1.50 | yes | 474 ± 5 | 94.8 | 89.2 ± 0 | 4.48 ± 0.36 | 28.4 ± 0.3 | 6.40 ± 0.58 |
|    |        |      | no  | 449 ± 6 | 89.8 | 91.1 ± 0.1 | 8.91 ± 0.14 | 51.7 ± 0.7 | 5.79 ± 0.01 |
| 90[b] | 0.4781 | 1.62 | yes | 914 | 183.0 | 52.0 ± 0.5 | 1.17 ± 0.05 | 7.46 ± 0.04 | 6.38 ± 0.23 |
|       |        |      | no  | 792 | 158.0 | 57.2 ± 0.5 | 5.93 ± 0.02 | 33.3 ± 0.4 | 5.62 ± 0.08 |

[a] Calculated as g PP/gm $TiCl_3 \cdot \frac{1}{3} AlCl_3$.
[b] Polymerization time at 90°C was only 4 h; the reported yield values are linearly extrapolated to 5 h.

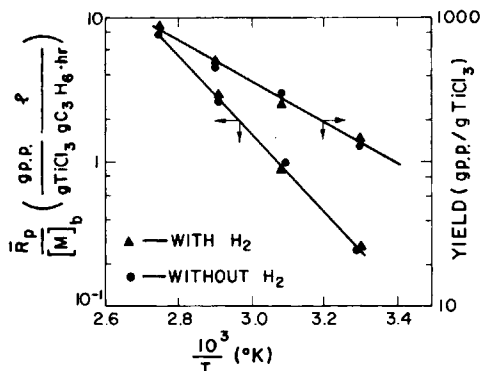Fig. 3. Arrhenius plot of the average polymerization rate and catalyst yield. (▲) With $H_2$, (●) without $H_2$.

The yield of polymer, plotted in Figure 3, shows almost straight line dependence on an Arrhenius plot. This data may be used to estimate an overall activation energy for the polymerization. Let us assume an approximate mass-action kinetic rate expression of the form

$$R_p = k_p(T)[M]_s[C^*] \tag{1}$$

where $R_p$ is the rate of polymerization (g/g cat·s), $[M]_s$ the propylene concentration at the catalyst surface (mol/L), and $[C^*]$ the concentration of active sites for polymerization (mol/g cat). Here $k_p$ is the kinetic rate constant for polymerization at the surface. Obviously $[C^*]$ depends on the type of catalyst used, the number of sites activated, etc. Similarly, $[M]_s$ will depend on the propylene concentration in the bulk slurry liquid $[M]_b$ as well as any diffusion limitations in the polymer particles. It is reasonable to approximate $[C^*]$ and $[M]_s$ by the relations

$$[C^*] = k_c(T)[C^*]_0 \tag{2}$$

$$[M]_s = k_m[M]_b \tag{3}$$

where $[C^*]_0$ is the maximum number of active sites available and $k_c(T)$ is the fraction actually active at any temperature $T$. Similarly, $[M]_b$ is the bulk phase propylene concentration, and $k_m$ is some coefficient relating surface concentrations to bulk phase concentrations. In the case of diffusion limitations in the particle, $k_m$ will depend on the amount of polymer formed at any time $t$, and is thus time dependent. Substituting (2) and (3) into (1) yields
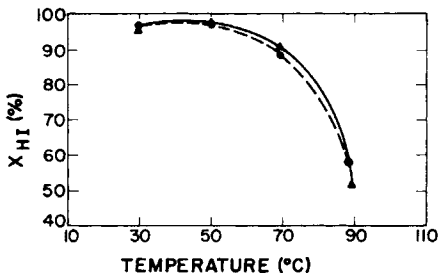


Fig. 4. Effect of polymerization temperature on the tacticity of the polymer. (——) Without $H_2$, (- - -) with $H_2$.
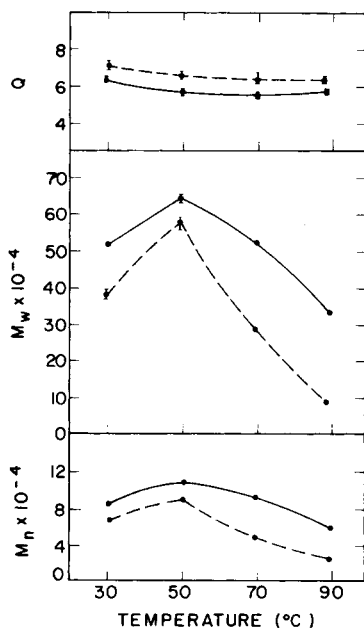
Fig. 5. Effect of polymerization temperature on the MWD of the polymer. (——) Without $H_2$, (---) with $H_2$.

$$R_p = k_{0v}(T)[C^*]_0[M]_b \tag{4}$$

where

$$k_{0v}(T) = k_p(T)k_c(T)k_m = \hat{k}_{0v}e^{-E_{0v}/RT} \tag{5}$$

is an overall rate constant for polymerization. Now recall that the polymer yield $Y$ and average rate $\overline{R}_p$ are given by

$$Y(t_f) = \int_0^{t_f} R_p \, dt = \int_0^{t_f} k_{0v}(T)[C^*]_0[M]_b \, dt \tag{6}$$

$$\overline{R}_p = Y(t_f)/t_f \tag{7}$$

which under constant temperature and constant bulk phase conditions may be rewritten

$$\overline{R}_p = \frac{Y(t_f)}{t_f} = \frac{[M]_b e^{-E_{0v}/RT}}{t_f} \int_0^{t_f} k_{0v}[C^*]_0 \, dt \tag{8}$$

or

$$\ln\left(\frac{\overline{R}_p}{[M]_b}\right) = \frac{-E_{0v}}{RT} + \ln\left(\frac{1}{t_f} \int_0^{t_f} k_{0v}[C^*]_0 \, dt\right) \tag{9}$$

Because the solubility of propylene in $n$-heptane depends strongly on temperature (cf. Table II), this effect must be included in eq. (9). An Arrhenius plot of eq. (9) (cf. Fig. 3) gives a value of $E_{0v} = 11.2$ kcal/g-mole which seems independent of whether or not $H_2$ was added. This value is in quite reasonable agreement with previous values reported for this polymerization (e.g., 12 kcal/g·mol,[39] 13 kcal/g·mol,[40] 11 kcal/g·mol,[29] and 10.3 kcal/g·mol.[41] The very good Arrhenius dependence of the average rate shown in Figure 3 suggests that there

is not a transition between kinetic and diffusion regimes over the temperature range studied. In addition, the polymer yields obtained here are compared to those reported by other workers for similar operating conditions and similar catalysts.[29,42–47] The minor variations among workers are thought to be due to differences in catalyst preparation methods, different Al/Ti ratios, and different slurry liquids.
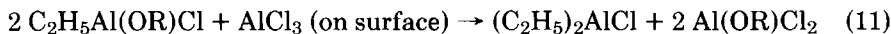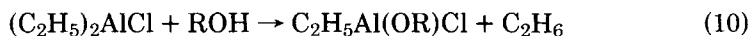
As illustrated in Figure 4, the tacticity of the polymer product increased slightly from 30°C to 50°C and then decreased sharply with polymerization temperature for polymerization above ~60–70°C. A similar slight increase in tacticity was also observed in the temperature range of 25–50°C with $TiCl_3/AlEt_2H$ catalyst system by Tamura et al.[48] The decrease in tacticity at higher temperatures is not unexpected because such effects are observed in many other polymer systems and are likely due to the higher rate of random monomer insertion relative to the rate of coordinated insertion at these higher temperatures. Such "hurried" insertion clearly favors atactic polymer formation.

Figure 5 shows the effect of polymerization temperature on the MWD. Note that there is a peak in $M_n$ and $M_w$ at about 50°C, but the polydispersity $Q$ is about 5–6 and is almost independent of the polymerization temperature. The maximum in $M_n$ at about 40–50°C is similar to that found in the case of 4-methylpentene-1 polymerization with $VCl_3/AlEt_3$ catalyst.[28] It is supposed that the higher activation energy of the chain transfer reaction tends to lower the degree of polymerization at elevated temperatures. The very slight narrowing of the MWD with increasing temperature agrees with the experimental observations by other workers.[23,40]

### Effect of Catalyst Poisons

In order to determine the influence of catalyst poisons on the polymerization yield and polymer properties, one of three catalyst poisons (isobutyl alcohol, phenol, trichloroacetic acid) was added about 25 min before the start of the polymerization. The results are tabulated in Table III.

The effect of adding isobutyl alcohol is to reduce polymer tacticity, slightly decrease the polymer molecular weight, and (in the presence of $H_2$) to increase polymer yield. This rate increase is consistent with the results reported by Masuda and Takami,[43] who added ethanol. However, these workers reported no significant decrease in tacticity. It is suggested[43] that the alcohol added reacts with the aluminum alkyl as follows:

$$(C_2H_5)_2AlCl + ROH \rightarrow C_2H_5Al(OR)Cl + C_2H_6 \qquad (10)$$

$$2\ C_2H_5Al(OR)Cl + AlCl_3\ (on\ surface) \rightarrow (C_2H_5)_2AlCl + 2\ Al(OR)Cl_2 \quad (11)$$

This effectively produces a "different" cocatalyst than DEAC, and the results (changed yield and tacticity) are similar to those observed with variations in cocatalyst.

In contrast to the case of isobutyl alcohol, the addition of phenol had very little effect on polymer yield or tacticity, but did decrease molecular weight somewhat in the presence of $H_2$ compared with polymerization without any poisons. Similar results are reported[49] for ethylene polymerization with a Ziegler catalyst to which a small amount of phenol was added. However, the polymer yields in the presence of $H_2$ turned out to be significantly enhanced compared with the

TABLE III

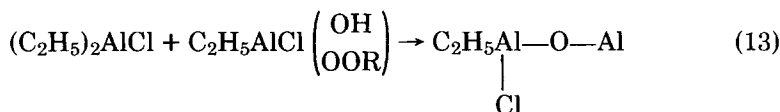Influence of Catalyst Poison on Polymer Yield and Properties (Polymerization under Standard Conditions at 70°C)
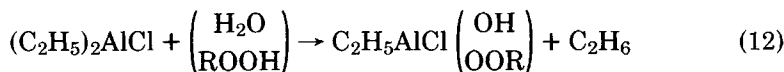
| Catalyst poison | $[X]_b$ (mol/L) | $H_2$ added | Yield[b] (g PP/g Ti cat) | Average rate (g PP/g Ti cat·h) | Tacticity $X_{HI}$ (%) | $M_n$ × 10⁻⁴ | $M_w$ × 10⁻⁴ | $Q = M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| None | — | yes | 474 ± 5 | 94.8 | 89.2 ± 0 | 4.48 ± 0.36 | 28.4 ± 0.3 | 6.40 ± 0.58 |
| | — | no | 449 ± 6 | 89.8 | 91.1 ± 0.1 | 8.91 ± 0.14 | 51.7 ± 0.7 | 5.79 ± 0.01 |
| Isobutyl alcohol | 7.5 × 10⁻³ | yes | 616 | 123 | 79.8 | 3.62 ± 0.13 | 28.1 ± 0.7 | 7.75 ± 0.10 |
| | | no | 381 | 76.2 | 81.1 ± 0.7 | 7.36 ± 0.04 | 46.8 ± 0 | 6.35 ± 0.04 |
| Phenol | 7.5 × 10⁻³ | yes | 479 | 95.8 | 90.8 ± 0.3 | 3.27 ± 0.04 | 21.0 ± 1.5 | 6.44 ± 0.39 |
| | | no | 342 | 68.4 | 91.2 ± 0.2 | 5.94 ± 0.61 | 36.4 ± 2.5 | 6.16 ± 0.21 |
| Trichloro acetic acid | 7.5 × 10⁻³ | yes | 11.1 | 2.22 | 91.6 | 4.78 ± 0.42 | 33.7 ± 1.0 | 7.6 ± 0.4 |
| | | no | 13.8 | 2.76 | 93.2 | 4.76 ± 0.06 | 59.9 ± 2.2 | 12.6 ± 0.3 |

[a] Concentrations of poison in $n$-heptane.
[b] Calculated as g PP/g $TiCl_3 \cdot \frac{1}{3} AlCl_3$.

cases in the absence of $H_2$ when isobutyl alcohol and phenol were added. Although the exact cause of this rate increase with $H_2$ is not completely understood at the present time, it can be postulated that the frequent chain transfer, when $H_2$ is added, leads to favorable interactions between additive molecules of isobutyl alcohol or phenol and $H_2$ at the catalyst surface.

The strongest effect was observed for the case of trichloroacetic acid addition. Polymer yield decreased dramatically, but tacticity remained high. This is in agreement with the work of Shikata et al.,[50] who report that for ($—COO—/TiCl_3$) ratios greater than 0.5, the polymerization rate is sharply decreased. With $TiCl_3$ and DEAC catalyst systems, catalyst activity is known to decrease by increasing the acidity of additives.[49] The influence of the acid is thought to be similar to that for water, i.e.,

$$(C_2H_5)_2AlCl + \binom{H_2O}{ROOH} \rightarrow C_2H_5AlCl\binom{OH}{OOR} + C_2H_6 \tag{12}$$

$$(C_2H_5)_2AlCl + C_2H_5AlCl\binom{OH}{OOR} \rightarrow \underset{\underset{Cl}{|}}{C_2H_5Al—O—Al} \tag{13}$$

Other destructive reactions with the transition metal compounds may also take place to deactivate the catalyst, e.g.,

$$TiCl_3 + \binom{H_2O}{ROOH} \rightarrow \binom{HO—TiCl_2}{ROO—TiCl_2} + HCl \tag{14}$$
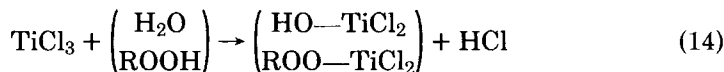
It has been suggested in patients[51,52] that the addition of these poisons should narrow the MWD of polyolefins by preferentially poisoning the most active sites on the catalyst. However, our results do not indicate any conclusive evidence that these poisons diminish the value $Q$ over the case without added poisons. In fact, for the case of trichloroacetic acid, the MWD was significantly broadened.

### Effect of Slurry Liquid

It has been suggested for the polymerization of ethylene[53] that when the polymer is soluble in the slurry liquid, the polymer MWD is considerably narrower. To study this effect in the polymerization of propylene, experiments were carried out with five different slurry liquids with varying solubility parameters $\delta$ (cf. Table IV). Hydrogen was added to all runs and the slurry liquid was a 50/50 mixture (by volume) of $n$-heptane and the noted compound.

In order to interpret solubility effects, the values of $\delta$ for the various slurry liquids must be compared with the solubility parameter $\delta$ for polypropylene. However, there is considerable disagreement in the literature regarding the value of $\delta$ for polypropylene. The Polymer Handbook[54] quotes values of $\delta \approx 9.2$–$9.4$, which appear to be incorrect. Other sources (e.g., Refs. 55–58) seem to agree that the value should be $\delta \approx 8.1$. Independent calculations[59] confirm this later value.

The solubilities of monomer and $H_2$ in the various slurry liquids were determined from a thermodynamic analysis[59] and are tabulated in Tables II and IV. The approach used was a modification of the Chao–Seader method,[60] employing

TABLE IV
Effect of Slurry Liquid on the Polymerization at 70°C; $H_2$ Added in Each Case

| Slurry liquid | Component $\delta$[a] $(\mathrm{cal/cm^3})^{1/2}$ | 50/50[b] mixture $\delta$ $(\mathrm{cal/cm^3})^{1/2}$ | $[M]$[b] (mol/L) | $[H_2] \times 10^3$ (mol/L) | Yield (g PP/g Ti cat) | Yield $[M]$[b] (g PP·L/mol·g Ti cat) | Tacticity $X_{HI}$ (%) | $M_n \times 10^{-4}$ | $M_w \times 10^{-4}$ | $Q = M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| n-Heptane | 7.4 | 7.4 | 0.8075 | 1.50 | 474 ± 5 | 587 ± 6 | 89.2 ± 0 | 4.48 ± 0.36 | 28.4 ± 0.3 | 6.40 ± 0.58 |
| Decane–heptane | 7.7 | 7.5 | 0.7090 | 1.36 | 546 ± 17 | 770 ± 24 | 93.7 ± 0.8 | 3.99 ± 0.16 | 27.2 ± 1.8 | 6.81 ± 0.24 |
| Cyclohexane–heptane | 8.2 | 7.8 | 0.8340 | 1.50 | 371 ± 34 | 445 ± 40 | 89.0 ± 0.6 | 4.43 ± 0.24 | 22.6 ± 0.9 | 5.12 ± 0.29 |
| Decalin–heptane | 8.8 | 8.1 | 0.6787 | 1.20 | 310 ± 50 | 457 ± 73 | 91.9 ± 0.7 | 4.26 ± 0.31 | 24.6 ± 0.7 | 5.82 ± 0.51 |
| Tetralin–heptane | 9.5 | 8.4 | 0.6210 | 1.09 | 96.0 ± 7.0 | 155 ± 11 | 96.5 ± 0.5 | 3.56 ± 0.24 | 20.8 ± 1.0 | 5.88 ± 0.33 |

[a] Refs. 54, 55, 60.
[b] Calculated from $\delta_{mix} = \nu_1\delta_1 + \nu_2\delta_2$, where $\nu_1, \nu_2$ are volume fractions of each component.

solubility parameters for propylene and hydrogen of $\delta = 6.43$ and $\delta = 3.25$, respectively. Space limitations do not allow a complete description of the analysis here, but more details will be provided in a later paper in this series and can be found in Ref. 59.

The polymerization results are tabulated in Table IV and illustrated in Figures
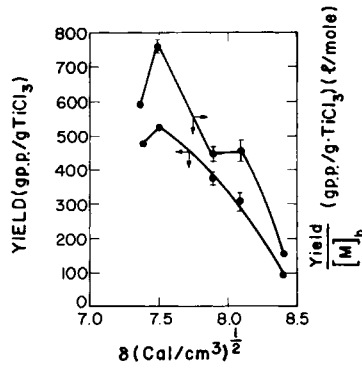


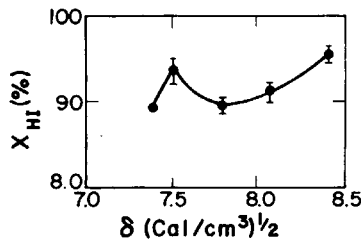Fig. 6. Influence of slurry liquid solubility parameter on the polymerization yield.



Fig. 7. Influence of slurry liquid solubility parameter on the tacticity of the polymer.
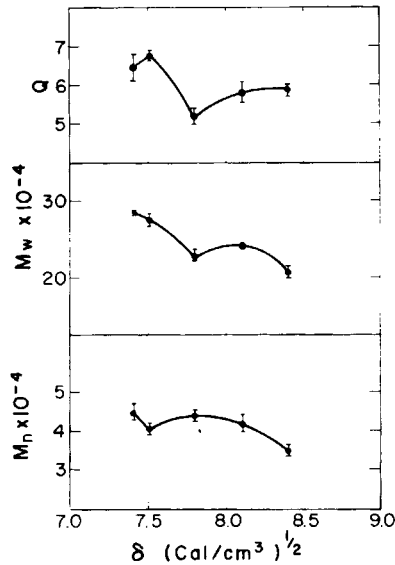


Fig. 8. Influence of slurry liquid solubility parameter on the MWD of the polymer.

6–8. The trends with $\delta$ seem to be quite clear except for the case of the $n$-heptane/decane slurry liquid. This mixture seems to have extraordinarily high yield and tacticity for its value of $\delta$. Duplicate runs of the polymerization and all of the analysis were carried out so that the result appears to be real. At present we have no satisfactory explanation for this behavior. It may be that $n$-decane has some beneficial chemical rate in the kinetics which makes it an improvement over the other slurry liquids tested. Because of the singular behavior of the $n$-decane slurry liquid, the discussion which follows will be largely independent of this case.

For the experiments shown, the measured polymer yield falls dramatically as the value of the solubility parameter of the slurry liquid approaches the solubility parameter value for propylene. This is likely due to increased dissolution of polymer (during polymerization) for those cases.

The measured tacticity of the polymer increases as the solubility parameter of the slurry liquid (with the exception of $n$-decane) approaches that of polypropylene. The higher apparent tacticity at the larger values of $\delta$ coupled with the lower yields are probably due to the dissolution of both atactic and isotactic polymer into the slurry liquid during polymerization, producing artificially low yields. The atactic polymer is more easily dissolved by the slurry liquid; thus later $n$-heptane extraction of the polymer will indicate higher tacticity. Absolute resolution of this question would require careful analysis of the polymer content of the slurry liquid, which was not done. The high tacticity coupled with the high yield for decane/$n$-heptane mixtures is most interesting. This suggests that such mixtures may have improved properties over heptane alone as a slurry liquid; however we, as yet, do not understand the exact mechanism.

The influence of slurry liquid on the MWD of the polymer may be seen in Figure 8. There appears to be a slight maximum in the number average molecular weight $M_n$ at $\delta \approx 7.8$–8.1. This may be shown to follow the propylene solubility behavior shown in Table IV, indicating that propylene concentration in the slurry liquid is the determining factor for $M_n$ in these experiments. There is also a pronounced narrowing of the MWD in the range $\delta = 7.8$–8.1. This may be due to improved solubility of the polypropylene and reduced diffusion resistance for the monomer as the polymer builds up. However, diffusion resistance for these runs is expected to be small so that the interpretation must remain equivocal. Nevertheless, the value of polydispersity, $Q = 5.1$, for the cyclohexane-heptane slurry ($\delta = 7.8$), was the lowest value noted in all of our experiments. Hence the results would be consistent with the view that diffusion limitations can account for some of the MWD broadening observed.

## CONCLUDING REMARKS

An experimental study has been carried out to determine the influence of temperature, catalyst poisons, and type of slurry liquid on polypropylene yield, tacticity, and MWD. The polymerization was carried out under relatively low pressure (60 psig) so that catalyst yields were relatively low and diffusion limitations likely small. Nevertheless, polydispersities of the polymer ranged from 5.0 to 12.0 depending on polymerization conditions, with most of the polymer having polydispersities of 6–7. Tacticity was generally high for lower poly-

merization temperatures and decreased rapidly for polymerization above 70°C. Polymer molecular weight reached a maximum value around 50°C and decreased with increasing temperature thereafter. Polymerization rate and yields increase with temperature with an overall activation energy of approximately 11.2 kcal/g·mol.

Catalyst "poisons" seemed not to have large effects on the yields except for trichloroacetic acid which sharply reduced catalyst yields. Both phenol and isobutyl alcohol showed only 15–20% decrease in yield without $H_2$ and no decrease or even an increase in yield with $H_2$ present (in the case of isobutyl alcohol). Tacticity was not strongly affected except for the case of isobutyl alcohol which decreased the isotactic content by more than 10%. Polymer number average molecular weight was reduced slightly by the catalyst poisons, but polydispersity was relatively unaffected except for the case of trichloroacetic acid where polydispersity increased dramatically without $H_2$ present. These results suggest that the more active catalyst sites are not poisoned preferentially over the catalyst as has been claimed by some.[51,52]

In all cases, $H_2$ addition was seen to reduce the number average molecular weight significantly and broaden the MWD slightly. This small amount of broadening may be due to the changing $[H_2]_b/[M]_b$ ratio over the course of the polymerization (as $H_2$ is consumed).

Perhaps the most interesting effects were seen as the slurry liquid was changed. As might be expected, better solvents for polypropylene reduced measured yield and increased measured tacticity because of polymer dissolution in the slurry liquid. However, a mixture of decane/heptane was found to depart from this trend and to increase both the yield and the isotactic content of the polymer. This suggests further experimental study. The narrowing of the MWD observed for slurry liquids which are the best solvents for the polymer seem to suggest that monomer diffusion is enhanced in these cases. This lends credibility to the proposal that such diffusion limitations may be partially responsible for MWD broadening.

Further experimental studies to explore the interesting cases uncovered here are now underway. Those results as well as detailed mathematical model predictions will appear in a forthcoming paper in this series.

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