

Propylene Polymerization in a Semibatch Slurry Reactor over Supported $\text{TiCl}_4 / \text{MgCl}_2 / \text{Ethyl Benzoate} / \text{Triethyl Aluminum}$ Catalyst. I. Catalytic Behavior

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Synopsis

High activity $\text{TiCl}_4 / \text{MgCl}_2 / \text{ethyl benzoate (EB)} / \text{triethyl aluminum (TEA)}$ catalysts for the polymerization of propylene were synthesized and characterized for particle size distribution and crystallinity. Polymerization was carried out in a semibatch, constant pressure slurry reactor. A correction for interfacial mass transfer was found to be necessary to relate the monomer feed rate to the instantaneous rate of polymerization. Without such a correction serious misinterpretation of rate data could result. Optimum productivity was observed with respect to the Al/Ti ratio. Similar behavior was observed with polymerization temperature. Isotacticity increased with polymerization temperature and decreased with Al/Ti ratio. The addition of a small amount of 2,2,6,6-tetramethylpiperidine increased the percentage of isotactic polypropylene to 98% without significantly affecting productivity.

INTRODUCTION

Since the development of supported catalysts for propylene polymerization, a great deal of information has appeared in the patent literature. A detailed summary of the patents granted up to 1981 was reported by Taylor¹ and Choi and Ray,² and a general review of historical development of both supported and unsupported catalysts for propylene polymerization was given by Pino and Mulhaupt.³ More recently, Dumas and Hsu⁴ have reviewed scientific developments of propylene polymerization over supported catalyst.

Supported catalysts are more active than conventional unsupported catalysts by at least an order of magnitude, and under certain operating conditions, they can produce polypropylene with a very high composition of isotactic polymer. Unfortunately, optimum polymerization conditions (temperature and Al/Ti ratio) for activity do not coincide with those for stereospecificity. Even with the addition of electron donors where the stereospecificity can be enhanced, they usually have an adverse effect on activity. Another manifestation of the catalyst system is the rapid deactivation of catalyst with polymerization time. The understanding of the catalytic reactions of the supported catalyst is very limited, and only a limited number of

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publications have emerged in the open literature which explore the fundamentals of this system.

Historically, depending on their particular backgrounds, various investigators have applied entirely different approaches in trying to elucidate the fundamentals of stereospecific olefin polymerization. Some researchers have studied the structure and stereochemistry of synthesized polymers; while others have investigated the structure of the catalyst by spectroscopic techniques, and in the case of heterogeneous catalyst, x-ray diffraction techniques as well. Another approach has involved developing various kinetic models based on assumptions concerning the reaction mechanism, and then fitting experimental polymerization data to these models. Statistical analysis can be used to accept or reject certain kinetic assumptions, which in turn enables us to identify the model which best describes the reaction mechanism.

In this investigation, a kinetic study of propylene polymerization with supported catalyst was undertaken. Experimentally, this involved preparing and characterizing various $\text{TiCl}_4/\text{MgCl}_2/\text{EB}/\text{TEA}$ catalysts (EB = ethylbenzoate; TEA = triethylaluminum). Also, a semibatch slurry reactor system was chosen to conduct polymerizations with these catalysts at a constant pressure. By measuring the instantaneous feed rate of monomer to the reactor, the instantaneous polymerization rate could be determined. However, it was found that mass transfer limitations across the gas-liquid interphase had to be considered. In this article, a method was developed whereby the instantaneous monomer feed-rate could be corrected for mass transfer limitations to obtain the instantaneous rate of polymerization. The development of a kinetic model and the interpretation of data will be discussed in a subsequent publication.

EXPERIMENTAL

Supported catalyst was prepared by co-milling MgCl_2 with ethyl benzoate, refluxing the ground solid with TiCl_4 , and rinsing with *n*-heptane. This catalyst was characterized in terms of titanium content using a colorimetric method, particle size distribution with an aerodynamic particle sizer, and crystal structure by x-ray diffraction. Polymerizations of propylene were carried out with this catalyst in a semibatch, slurry reactor which was operated at a constant pressure. Triethylaluminum (TEA) was used as a cocatalyst. The polymerization rate was determined by measuring the propylene feed rate to the reactor. The isotactic index of the polymer was determined by soxhlet extractions with boiling *n*-heptane. Scanning electron microscopy was used to examine the product morphology.

Materials

Chemical purity propylene was obtained from Matheson Corp. (Whitby, Ontario). It was dried by passing through a drierite column and a column containing type 3 Å molecular sieves.

Technical-grade *n*-heptane, from Fisher Scientific Ltd. (Fair, NJ) was dried with type 4 Å molecular sieves following a procedure similar to that sug-

gested by Ceausescu et al.⁵ The sieves were first activated by heating to 275°C in a helium stream for 2 h. The moisture content of the solvent was reduced to less than 10 ppm, as determined by gel chromatography analysis employing a method described previously by Dumas and Hsu.⁶

Pure-grade nitrogen, from Canox Ltd. (Kingston, Ontario) was passed through a drierite column to remove moisture. When used in the reactor, it was further purified by passing through two oxygen adsorbing columns, obtained from Alltech Associates (Deerfield, IL).

All of the other chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. These included: magnesium chloride, 98%; ethyl benzoate, 99+%; 2,2,6,6-tetramethylpiperidine, 99+%; and triethylaluminum, 1.0 *M* solution in hexanes.

Catalyst Synthesis

All catalyst synthesis steps were carried out under a dry nitrogen atmosphere. Magnesium chloride and ethyl benzoate (usually in a 6:1 molar ratio) were co-milled in a 1.1-L porcelain mill using curundum two grinding cylinders for a period of 120 h. After milling, the powder was refluxed with excess TiCl_4 for 2 h at 80°C and subsequently rinsed with an excess amount of *n*-heptane. The detailed procedure can be found elsewhere.⁷

The catalyst particle size distribution was analyzed with an APS33 aerodynamic particle sizer, from TSI Inc. (Minneapolis, MN). In order to prevent exposure to air, the catalyst was introduced to the instrument in a nitrogen stream.

The titanium content of the catalyst was determined using a colorimetric method.⁸

The x-ray diffraction patterns for various catalyst samples were obtained with a CSS STOE STADI/2PL two circle powder diffractometer (Darmstadt, West Germany) operating in the Debye-Scherrer mode, using CuK radiation. Samples were packed into 1 mm diameter glass capillary tubes and sealed with epoxy resin, in the glove box under a nitrogen atmosphere.

Polymerization

Reactor System

A 250-mL autoclave, manufactured by Autoclave Engineers (Erie, PA) was used as a semibatch slurry reactor. The stainless steel reactor was equipped with a cooling coil, a thermocouple well, a 3.0-cm diameter, 6 flat-blade impeller, an injection port, and feed lines. Baffles were not employed and the propylene was not sparged through the slurry but, instead, entered the reactor through the cover plate. The sparger was found to be easily plugged. A "magnedrive" magnetic stirrer was used to avoid possible contamination from leakage through the impeller seal. All polymerization runs were carried out with an impeller speed of 1360 rpm. The temperature was maintained within $\pm 0.2^\circ\text{C}$ of the desired value.

The instantaneous rate of polymerization was obtained by monitoring the instantaneous monomer feed rate continuously throughout a polymerization run using an electronic flowmeter.

Polymerization Procedure

One of the major concerns with this type of polymerization is contamination of the system with impurities such as oxygen or moisture, which will destroy the catalyst activity. Therefore, TEA solution was added first to *n*-heptane, saturated with propylene, before the addition of catalyst. In this way, the TEA would scavenge any oxygen or moisture left in the solvent.

To introduce a known mass of catalyst powder to the pressurized reactor, a special type of catalyst cartridge was developed. Under a nitrogen atmosphere, a known mass of catalyst was packed into a 6-mm OD \times 4-mm ID \times 9-cm long polyethylene tube. This tube was then sealed at both ends with specially fabricated Teflon plugs. Because this tube had also been fitted with "Swagelok" type compression fittings, one end could be mated to the reactor (through a drilled-out fitting), and the other end to a ball valve. Catalyst addition involved: opening the ball valve; forcing the rod through the valve and cartridge, to push the first Teflon plug and the catalyst into the reactor; withdrawing the rod; and then closing the ball valve as a precaution in case the Teflon plug remaining in the tube should also drop into the reactor during polymerization.

Even though the conditions for catalyst preparation were carefully controlled, the titanium composition still varied from batch to batch as shown in Table I. To avoid the possible effect of the variation, catalyst samples were taken from the same batch for the study of a particular operating variable.

In studying the effects of Al/Ti ratio a series of experiments were conducted at 50°C using catalyst batch #3, with Al/Ti molar ratios ranging from 2 to 90. In most cases, 40 mg of catalyst were used and various amounts of TEA solution were added to obtain the desired Al/Ti ratio. Catalyst batch #4 was used for the study of temperature effects with an Al/Ti ratio of 25 and a temperature range of 10 to 70°C. Depending on the reactivity at the particular temperature being investigated, either 40, 60, or 80 mg of catalyst were used. The effects of additive, tetramethyl piperidine (TMPIP) on kinetic parameters were studied at 50°C and an Al/Ti ratio of 50, using catalyst batch #5 with 60 mg of catalyst per run. The amount of TMPIP added to the reactor ranged from 0 to 450 μ L and corresponded to a TMPIP/Ti range of 0

TABLE I
Titanium Composition of Catalysts Ballmilled for 120 h

Catalyst batch no.	Ti composition %Ti by wt	Standard deviation %Ti by wt
1	6.2	—
2	7.3	—
3	7.8	0.2 ($n = 3$)
4	4.9	0.2 ($n = 2$)
5	4.3	0.2 ($n = 4$)

to 45.5. The additive was introduced to the reactor after TEA followed immediately by the addition of the catalyst. The formation of TMPIP-TEA complex is therefore unlikely. In all runs, the pressure in the reactor was kept at $1.18 \pm .01$ bar. Each experimental run usually lasted 90 min.

Gas-Liquid Interfacial Mass Transfer

Prior to the polymerization experiment, a mass transfer study was carried out to quantitatively assess the gas to liquid phase mass transfer of propylene gas in the reactor. The procedure involved sampling the liquid phase for propylene while simultaneously monitoring the rate of propylene gas absorption without using any catalyst.

A Varian 3700 gas chromatograph with a flame ionization detector was employed for propylene analyses. The column (0.4-m long \times 3-mm I.D., nickel) was packed with Porapak R (100–200 mesh). With helium as a carrier gas at a flow rate of 20 mL/min and an oven temperature of 60°C, the retention time for propylene was 75 s. Peaks were integrated with a Hewlett-Packard 3390A integrator. A 1.0 μ L liquid syringe, fitted with a Chaney adaptor, was used for liquid samples.

Propylene gas, at known temperature and pressure, was used to calibrate the chromatograph. A reinjection procedure, described previously by Dumas and Hsu⁶ and Dumas⁹ was employed for gas sampling.

Kinetic Data Collection Using a Semibatch Slurry Reactor

Gas-Liquid Interfacial Mass Transfer

Within the reactor, propylene in the gas phase must be absorbed into the solvent (*n*-heptane) before it can reach the catalyst surface to be polymerized. Therefore the interfacial mass transfer resistances of gas–liquid and liquid–solid must be examined. However, previous investigations^{10–13} have shown that the polypropylene layer surrounding the catalyst particles likely does not create a diffusional barrier. In this work the number-average molecular weights of the polypropylene obtained range from 30,000 to 60,000, which is comparable to those obtained by previous investigators. Therefore, the mass transfer across the liquid–solid interface was not considered.

In this experiment, before catalyst was introduced to the reactor to initiate polymerization, the liquid phase was saturated with propylene. However, during the polymerization the propylene concentration in the slurry phase was found to remain below the equilibrium concentration. The magnitude of this resulting concentration difference between the equilibrium and actual monomer concentrations at any time during polymerization will depend upon both the polymerization rate and the mass transfer rate. Figure 1 illustrates this transience in monomer concentration for a typical run. Various changes in impeller design, agitation speed, baffling, and gas sparging were made in an effort to eliminate the mass transfer limitations which result in the transience in monomer concentration shown. However, these efforts did not completely eliminate the mass transfer limitations.

Nonconstant liquid phase monomer concentration during a polymerization run results in two major consequences: First, the instantaneous rate of

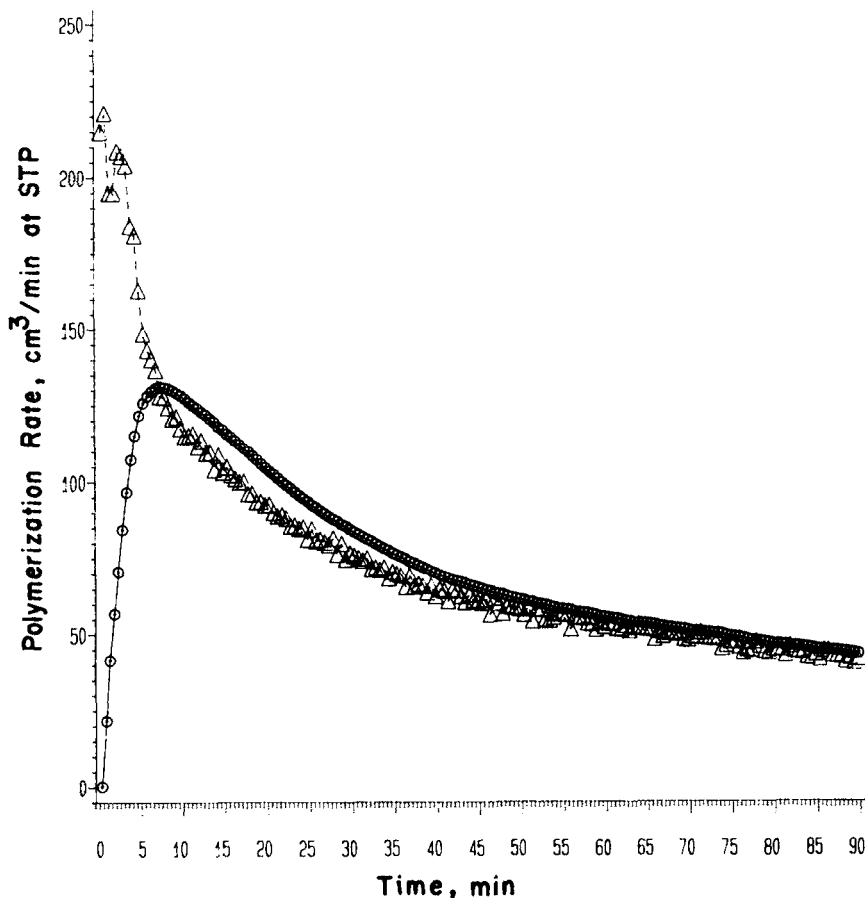


Fig. 1. Propylene flow rate as measured by the flowmeter (circles) as compared with the corrected polymerization rate (triangles). Polymerization conditions: 50°C, $[Ti] = 64.4 \mu\text{mol/L}$, $Al/Ti = 21.3$.

polymerization is a function of instantaneous monomer concentration. Therefore, to model the polymerization kinetics, the instantaneous monomer concentration must be determined for the entire run. Second, because the monomer concentration changes during a polymerization run, particularly during the early stage when the rate of polymerization is significantly higher than the rate of gas to liquid phase propylene mass transfer, the instantaneous propylene gas feed rate is not equal to the instantaneous rate of polymerization.

From a mass balance, the relationship between the polymerization rate and the monomer feed rate can be written as

$$R_p = -Vd[M]/dt + F_{\text{propylene}} \quad (1)$$

where R_p is the instantaneous rate of propylene polymerization, $F_{\text{propylene}}$ the experimentally measured propylene flow rate, V the volume of reaction mixture and $d[M]/dt$ the change of monomer concentration with time to t .

Since no mass transfer coefficient data for the polymerization system are available, we adopted an empirical approach to determine a correlation relating the propylene concentration as a function of propylene flow rate in heptane and temperature. A number of mass transfer runs were performed at 1.18 ± 0.01 bar pressure and at temperatures of 10, 20, 30, 40, 50, 55, 60, and 70°C, with replicate runs for each temperature, and the monomer concentration was then correlated with $F_{\text{propylene}}$ and T as a second-order polynomial. From regression analysis the model was shown to be adequate. The correlation was then used to calculate the monomer concentration at any given time from experimentally measured monomer flow rate and temperature in polymerization runs.

The correlation was obtained for propylene gas absorption into pure *n*-heptane. However, during polymerization propylene gas is absorbed not by pure *n*-heptane but by a slurry of *n*-heptane, catalyst, cocatalyst, and polypropylene. Polypropylene is insoluble in *n*-heptane at polymerization temperatures and so should not affect propylene solubility. To determine the effect of other components on gas absorption, mass transfer runs were performed using the reaction product slurries obtained after polymerization, instead of pure *n*-heptane. Two mass transfer runs were performed at 40°C, which contain 9 and 11 g of polypropylene. The 95% confidence intervals of the regression curves with and without polymer overlap. This implies that the experimental propylene mass transfer correlation obtained for pure *n*-heptane may also be applied to polymerization slurries containing *n*-heptane, catalyst, cocatalyst, and polypropylene.

Another consideration is the possible enhancement in gas absorption due to the polymerization reaction. If the catalytic activity is sufficiently high and its concentration in the reactor is also high, the rate of gas absorption would be greater than that predicted from the interfacial concentration gradient alone. Danckwerts¹⁴ suggested methods for quantifying this effect by calculating an enhancement factor, E , defined as the rate of gas absorption in the presence of reaction divided by the rate of absorption without reaction. Therefore, when E is greater than one, the reaction enhances the rate of gas absorption.

For this particular polymerization system, substitution of typical catalyst concentrations and activities into the Danckwerts' correlations indicated that the enhancement factor was not greater than 1.0. Although a significant degree of enhancement may have been expected with this high activity catalyst; because the amount of catalyst that was used was relatively small, the overall effect on enhancement was negligible. Therefore, the experimental propylene mass transfer correlation, obtained for pure *n*-heptane, can also be applied to the polymerizing slurry.

RESULTS AND DISCUSSION

Catalyst and Polymer Characterization

Catalyst Characterization Results

The particle size distribution for a typical batch of catalyst prepared is shown in Figure 2. It indicates a mean aerodynamic diameter of $\sim 2 \mu\text{m}$ and a maximum aerodynamic diameter of $\sim 8 \mu\text{m}$.

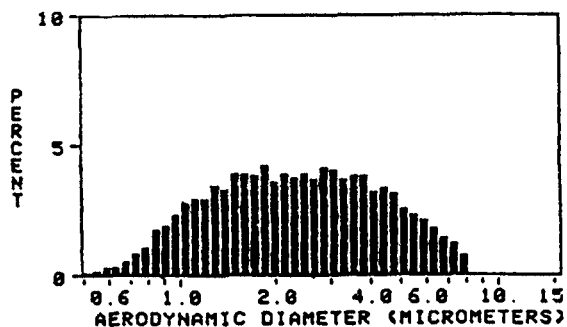


Fig. 2. Particle size distribution of catalyst in terms of aerodynamic diameter.

The composition of titanium for various catalysts ranged from 4.3 to 7.8% by weight, as shown in Table I. The precision of these determinations was reflected by typical standard errors of $\pm .2\%$ Ti by weight.

The effect of ball-milling time on the x-ray diffraction pattern of catalyst is shown in Figure 3. The MgCl_2 as received [Fig. 3(a)], shows strong reflections

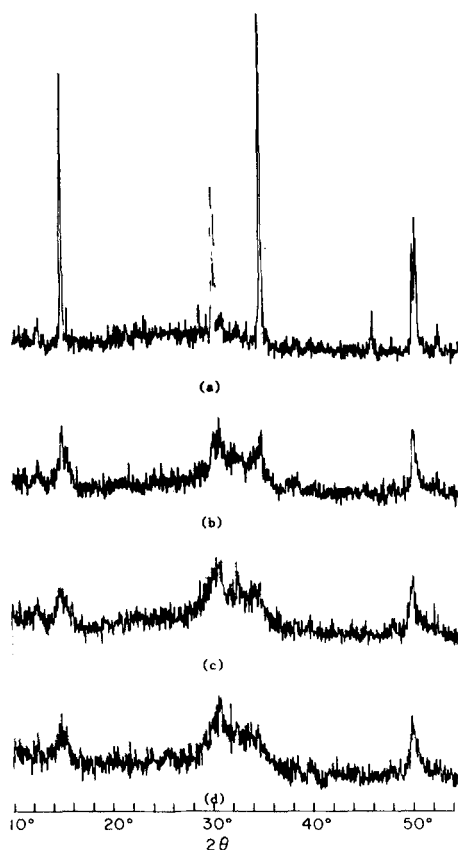


Fig. 3. Effect of ball-milling time on the x-ray diffraction pattern of a 6:1 molar ratio mixture of MgCl_2 and EB: (a) MgCl_2 as received; (b) MgCl_2/EB co-milled for 30 h; (c) co-milled for 70 h; and (d) co-milled for 100 h.

at $2\theta = 15.0^\circ$, 30.3° , 32.8° , and 50.1°C . Upon co-milling this MgCl_2 with EB in a 6:1 molar ratio for 30 h [Fig. 3(b)], the peaks broaden and diminish in height, indicating a decrease in crystallinity. Also, a broad halo forms in the 28°C to 35°C 2θ region. These effects of ball-milling have been observed by other investigators as well. They have interpreted these changes in terms of an increase in the composition of rotationally disordered MgCl_2 , as reviewed previously by Dumas and Hsu.⁴

Because of the relatively low signal to noise ratio, it is uncertain whether further milling up to 70 h [Fig. 3(c)] or 100 h [Fig. 3(d)] significantly affects crystallinity. However, as discussed previously by Dumas and Hsu,⁴ some authors have observed significant changes in crystallinity up to 60 or even 100 h of ball-milling time. This is likely because different investigators usually carry out their ball-milling with different types of equipment.

Figure 4(a) shows the effects of further treatment steps on catalyst material obtained after co-milling MgCl_2 and EB for 100 h. No significant changes were observed upon washing with *n*-heptane [Fig. 4(b)]. However, refluxing with excess TiCl_4 at 80°C for 2 h resulted in a new peak at $2\theta = 10.5^\circ$ [Fig. 4(c)]. To obtain more detail, the 10° to 20° portion of this pattern was rescanned using a much slower scanning speed [Fig. 4(d)]. This peak was not identified as belonging to any particular compound, but low 2θ values corre-

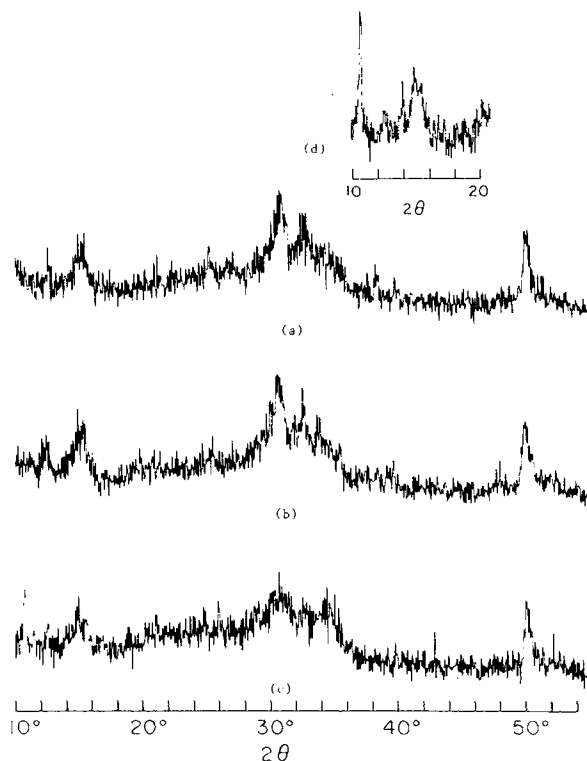


Fig. 4. Effect of catalyst preparation steps on the x-ray diffraction pattern of previously co-milled MgCl_2/EB : (a) co-milled for 100 h; (b) followed by rinsing with *n*-heptane; (c) followed by refluxing with TiCl_4 for 2 h at 80°C ; (d) same as (c) but rescanned at a much lower speed.

spond to relatively large unit cell dimensions which are typical of organic structures.

Polymer Characterization Results

Scanning electron photomicrographs of the polymer were taken using acceleration voltages of 2 and 20 kV. The sample was first sputter-coated with gold to reduce charging effects. The results are shown in Figures 5 and 6 at various magnifications. Figure 5 indicates that the product is composed mainly of agglomerations of spherical particles. These particles range in diameter from approximately 2 to 10 μm . Further magnification of the sample (Fig. 6) provides a better indication of the spherical nature of the particles.

The isotactic index (II) defined as the percentage of polypropylene insoluble in boiling *n*-heptane ranged from 88 to 98%, depending on the operating conditions. As shown in Figure 7, tacticity decreases with increasing Al/Ti ratio, whereas it increases with polymerization temperature (Fig. 8). Small amounts of TMPIP are particularly successful in increasing the isotactic index (Fig. 9).

Instantaneous Polymerization Rate

From the material balance of Eq. (1), it is evident that the instantaneous rate of polymerization can be obtained from the instantaneous monomer concentration and the instantaneous propylene feed rate to the reactor.

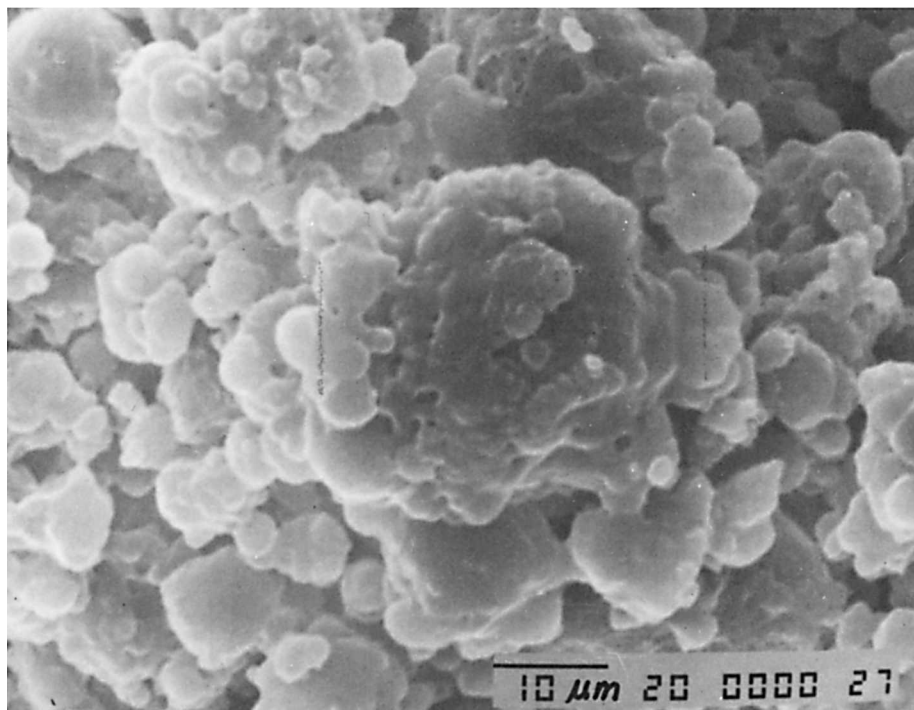


Fig. 5. Photomicrograph of polypropylene indicating agglomerations of different sized particles. Polymerization conditions: 50°C, $[\text{Ti}] = 53.9 \mu\text{mol/L}$, Al/Ti = 55.7.

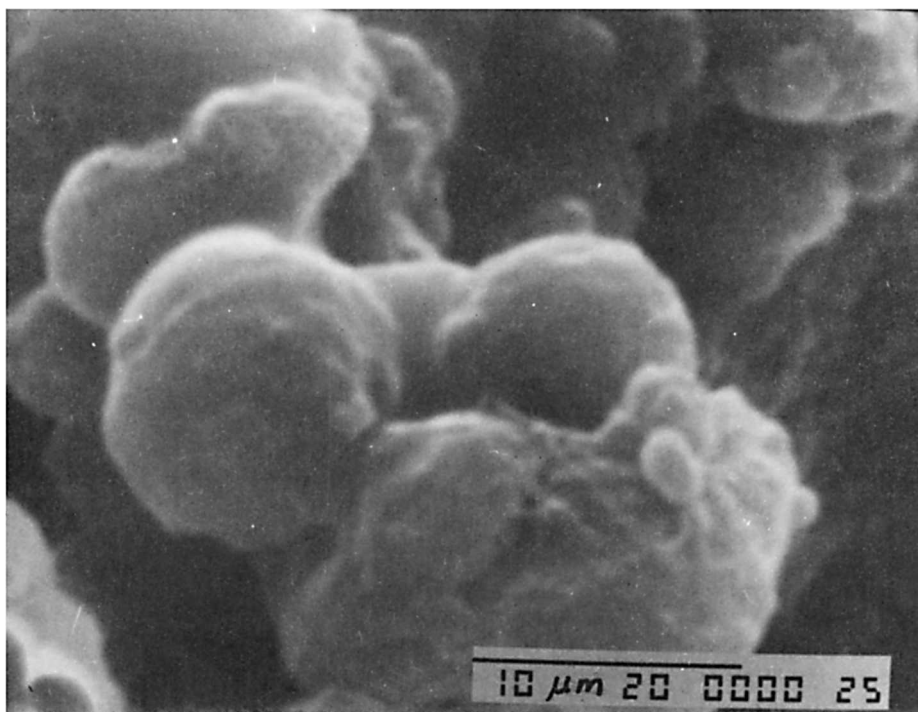


Fig. 6. Photomicrograph of polypropylene indicating the spherical nature of the particles. Polymerization conditions same as given in Figure 5.

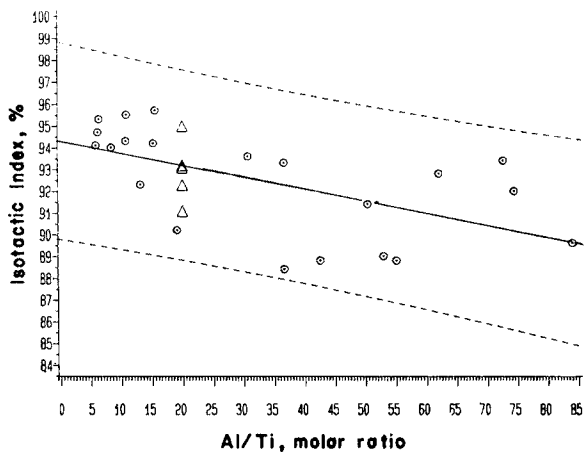


Fig. 7. Effect of Al/Ti on isotactic index for 90 min runs at 50°C. Triangles are for the catalyst #2 and circles for the catalyst #3. A regression line (solid) with 95% confidence limits (dotted lines) is also shown.

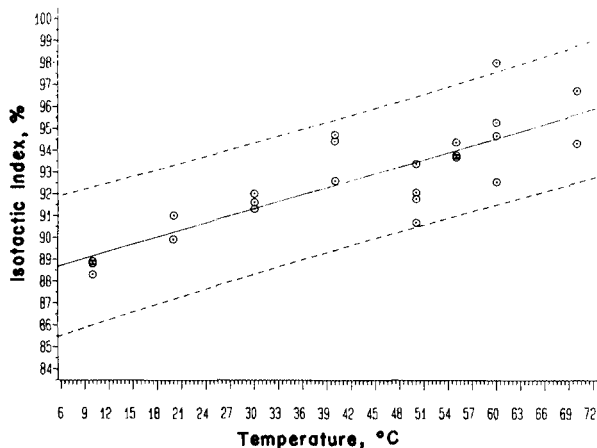


Fig. 8. Effect of temperature on isotactic index for 60 min runs at Al/Ti = 25. A regression line (solid) with 95% confidence limits (dotted lines) is also shown.

Because the instantaneous flow rate is measured and recorded continuously throughout a run and because the instantaneous monomer concentration can be calculated from the instantaneous flow rate, it is possible to obtain as many values of the instantaneous polymerization rate as desired such that the term $-d[M]/dt$ of Eq. (1) may be closely approximated by the term, $([M]_{t2} -$

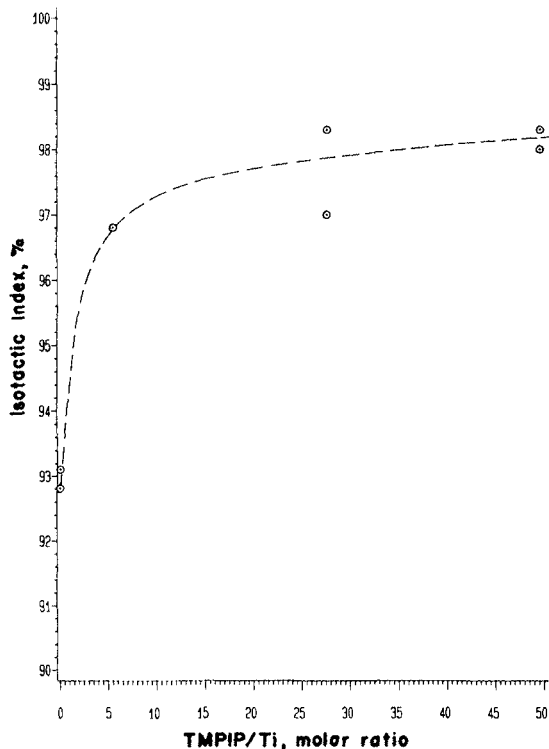


Fig. 9. Effect of TMPiP on tacticity at 50°C and Al/Ti = 50.

$[M]_{t_1})/(t_1 - t_2)$, where $[M]$ is calculated from monomer concentration correlation. Figure 1 is an example of an instantaneous rate of polymerization versus time curve (in triangles) obtained in this manner. The data points in circles are the direct measurements of propylene flow rate from the flowmeter. The effect of correction for the monomer concentration transience, is obvious, as shown in the figure. The concentration correction not only shift R_p values but also drastically affects the qualitative nature of the curve. Without performing the correction, it would have been concluded that an induction period was present at the start of this polymerization run. However after correction, the polymerization rate clearly indicates a continuous decrease in rate with polymerization time.

Forty-five experimental runs to obtain polymerization rate curves similar to that shown in Figure 1 were undertaken varying the polymerization temperature and the ratios of Al/Ti and TMP/IP/Ti. The Al/Ti ratio ranging from about 5 to 85 was investigated for its effects on polymerization. The temperature were varied from 20° to 60°C. Beyond 60°C we found difficulties of operating the reactor properly. In six experiments TMP/IP was added into the reaction mixture to study its effects on polymerization.

Effect of Al / Ti Ratio

The effect of Al/Ti ratio on productivity is shown in Figure 10. For a polymerization time of 90 min, an optimum productivity of approximately 6 kg polypropylene/g Ti was observed at an Al/Ti ratio of approximately 15. As reported previously by Dumas and Hsu,⁴ this type of optimum behavior

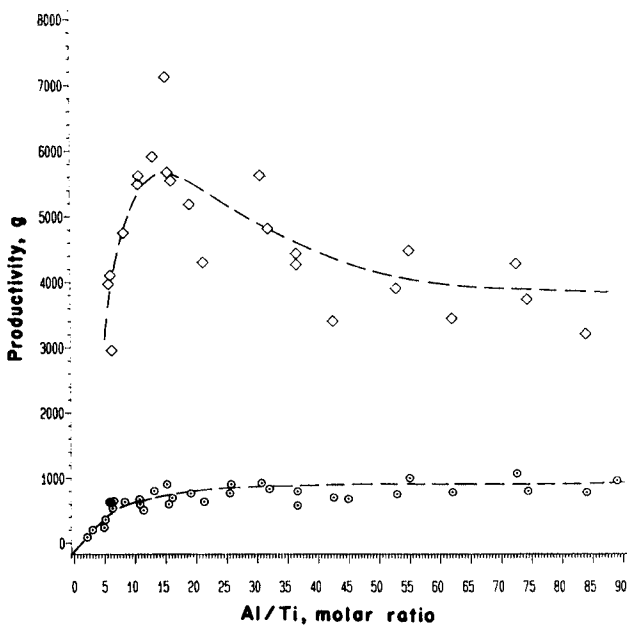


Fig. 10. Effect of Al/Ti on productivity (g PP/g Ti) measured at polymerization time of 5 min (circles) and 90 min (diamonds) and at 50°C.

has also been observed by other investigators. Depending on the system, optimum activity occurs at Al/Ti ratios ranging from 10 to 50. Keii et al¹⁵ have attempted to explain this optimum behavior in terms of adsorption isotherms. What was referred to as a linear form of the Langmuir-Hinshelwood mechanism was used to describe the surface coverage of catalyst by aluminum alkyl.

The concept of adsorption isotherms has been widely used in the field of heterogeneous catalysts. The underlying principle of this approach is based on the assumption that molecules must first adsorb onto the catalyst surface before they can react. An equilibrium will therefore exist between adsorbed molecules and those in the bulk phase. When more than one type of molecule is present, competition may occur for coverage of the catalyst surface. Burfield et al¹⁶ were among the first investigators to apply the concept of competitive adsorption to heterogeneous coordination polymerization. They applied the Hinshelwood mechanism and suggested that aluminum alkyl and monomer must compete for active sites. Both monomer and aluminum alkyl are required for polymerization, however, when the aluminum alkyl concentration becomes large, the number of active sites available for monomer adsorption is reduced, thereby decreasing the overall polymerization activity. Although this principle can be used to explain the optimum polymerization activity with respect to Al/Ti ratio, a number of points should also be considered.

1. In certain types of heterogeneous catalysts, such as those involving zeolites, the catalyst is porous, and therefore reactants must enter these pores before they can contact active sites and subsequently react. When more than one type of molecule is present, competition may exist for these active sites, because as long as a molecule is below a critical size range, it can enter and block a pore regardless of its chemical nature. Hence, the concepts of competitive adsorption and adsorption isotherms may be applied to these systems.

However, with this particular supported catalyst system, the catalyst is nonporous.¹⁷ Also, the active sites are complex organometallic structures which may not allow indiscriminate adsorption by any type of molecules. It seems more likely that molecules will attach to the complex through ligand formation rather than by simple adsorption. Steric factors may also play a role. According to the Cossee mechanism,¹⁸ the monomer must coordinate with the transition metal (in this case, titanium) before it can be inserted into the growing polymer chain. With this system, Ti is already coordinated with chlorine atoms of the MgCl₂ support, ethyl benzoate, and the growing polymer chain, so it would therefore seem difficult for a relatively bulky TEA molecule to find a spot to be adsorbed onto the titanium atom, thereby preventing monomer adsorption.

2. As shown in Figure 11, the addition of a relatively large amount of additional TEA solution after 62 min of polymerization did not result in any noticeable amount of catalytic deactivation, apart from the instantaneous pressure disturbance upon TEA solution injection. If TEA were in fact competing for sites with monomer, then a decrease in catalytic activity would have been expected.

3. Certain homogeneous polymerization systems also exhibit this optimum behavior observed by Hsu and co-workers^{19,20} with respect to Al/Ti ratio, even though adsorption is irrelevant in this case.

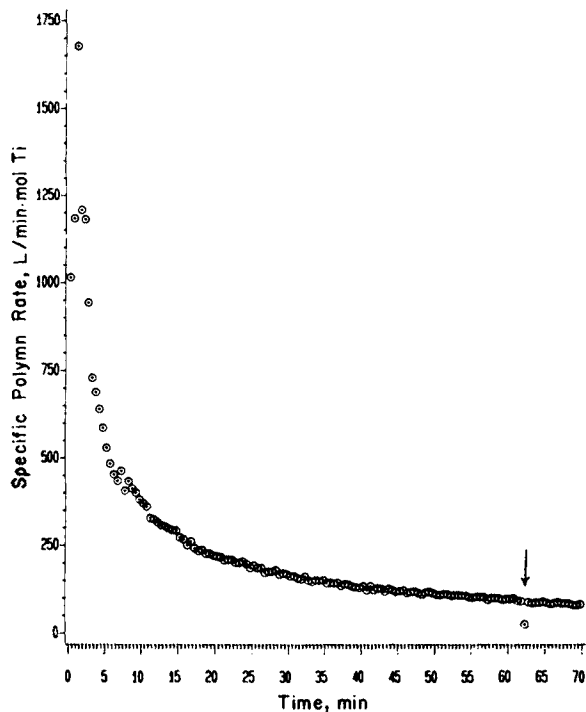


Fig. 11. Polymerization curve at 50°C, Al/Ti = 50 and 60 mg of Ti catalyst. 3.0 mL of additional TEA solution were added after 62 min of polymerization time. The specific rate is referred to the reaction mixture volume of 0.23 L.

4. As shown in Figure 10, for a polymerization time of 5 min, an optimum in productivity is not observed. Instead, productivity increases with Al/Ti ratio and eventually becomes relatively constant. Because there is no reason to assume that competitive adsorption should only take place during the later stages of polymerization, explanations other than competitive adsorption should be considered.

For supported catalysts it is believed there are more than a single type of active species of different activities. Sites of different activities should also be expected to have different rates of deactivation as well. Under the influence of operating conditions, such as Al/Ti ratio, these two opposing effects could very well lead to an optimum production of polymer. A quantitative analysis of this joint effect will be presented in Part II of this series with the development of kinetic model.²¹

Effect of Temperature

The effect of temperature on productivity is shown in Figure 12. For 60 min of polymerization time, an optimum in productivity is observed at approximately 50°C. The lower productivity at 70°C is not a result of kinetic phenomena alone. The polymer product was very sticky at this temperature and it agglomerated into one large mass which coated the impeller. Therefore, diffusional limitations would almost have certainly reduced productivity at this temperature. Using conventional type catalyst, Taylor¹ also observed this

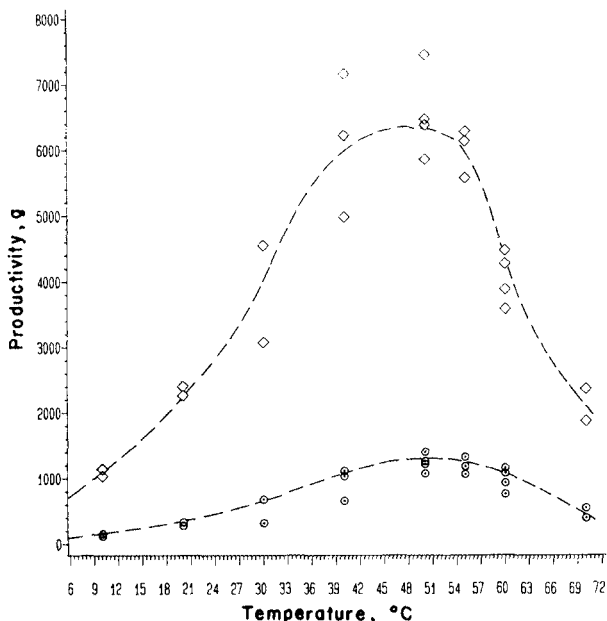


Fig. 12. Effect of temperature on productivity at Al/Ti = 25, where circles represent 5 min polymerization time and diamonds represent 60 min polymerization time.

agglomeration phenomenon, however in his case it occurred at 90°C. In this investigation, the problem occurred at a lower temperature because H₂ was not used as a chain transfer agent to reduce the molecular weight of the product. The data collected at 10°C are also unreliable because it was difficult to maintain the reactor at such a low temperature during polymerization.

Effect of 2,2,6,6-Tetramethylpiperidine on Polymerization

Compounds of Lewis base (electron donor), including many types of alcohols and esters, have been used as additives to improve the stereospecificity of supported catalyst for propylene polymerization. Unfortunately, their use often results in a decrease in productivity along with an increase in the composition of isotactic polymer.

Langer et al²² found that the Lewis base, 2,2,6,6-tetramethylpiperidine (TMPIP) was particularly successful in increasing the isotactic index with a relatively small decrease in productivity. They suggested that the electronic and steric properties of this molecule allow it to selectively poison atactic-specific sites. The decrease in activity associated with the use of additives may be a result of electron donor-alkyl aluminum side reactions which decrease the effective concentration of aluminum alkyl. Following this argument, Langer and co-workers suggested that highly sterically hindered electron donors and cocatalysts would be less susceptible to these side reactions.

As expected, our data (Fig. 9) show a significant increase in isotactic index by adding TMPIP to the system; however beyond TMPIP/Ti ratios of approximately 5, further improvement in the isotactic index is relatively small. The associated effect on productivity is shown in Figure 13. The

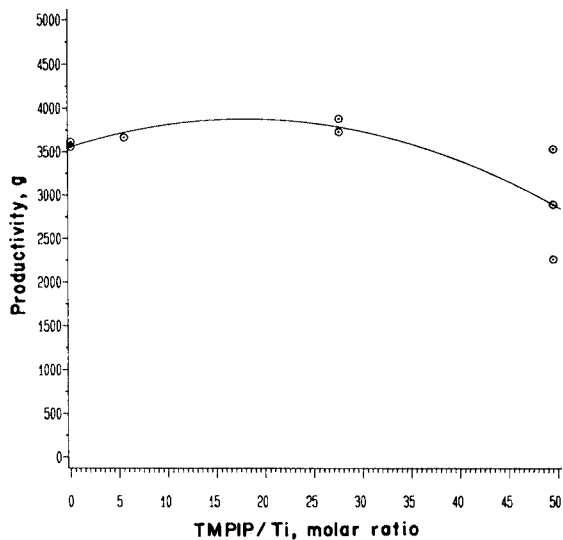


Fig. 13. Effect of TMPIP on productivity (g PP/g Ti) for 60 min runs at 50°C and Al/Ti = 50.

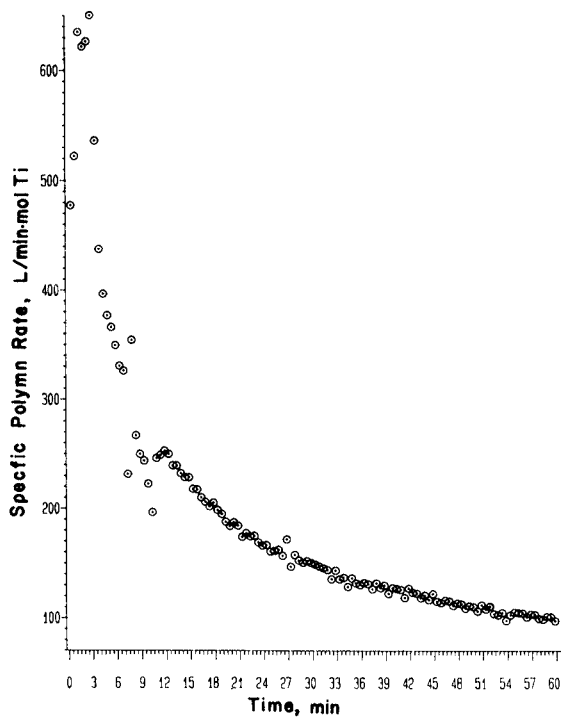


Fig. 14. Polymerization curve at 50°C and Al/Ti = 50 with 450 μ L of TMPIP added after 10 min polymerization. 60 mg of catalyst was used. The specific rate is referred to the reaction mixture volume of 0.23 L.

productivity is reduced only at relatively high TMPIP/Ti ratios; and interestingly, although the effect is not large, small amounts of TMPIP actually improve productivity. Perhaps a TMPIP-TEA side reaction decreases the effective TEA concentration resulting in an Al/Ti ratio closer to the optimum value of approximately 15. In practice, with an Al/Ti ratio of 50, a TMPIP/Ti ratio of approximately 25 would be desirable because the isotactic index would be increased significantly with no associated decrease in productivity.

As already discussed TMPIP improves tacticity by blocking atactic-specific sites; and when isotactic specific sites are also blocked, a significant reduction in productivity is observed. This relation was not what we observed in this work. Possible explanations resulted from the kinetic analysis will be given in Part II of this study.

An interesting effect was observed upon the addition of 450 μL of TMPIP, 10 min after the start of the polymerization, as shown in Figure 14. During the first few minutes following this addition, the instantaneous polymerization rate stopped decreasing and actually increased. This behavior suggests that TMPIP does much more than poison active sites. Perhaps TMPIP or a reaction product of TMPIP and TEA reacts with active centers to increase polymerization activity. Investigations into the actual chemical composition and structure of active centers would be useful in understanding this behavior.

CONCLUSION

The MgCl_2 -supported catalyst of $\text{TiCl}_4/\text{EB}/\text{TEA}$ synthesized in this study was characterized for the effects of milling on crystallinity and particle size distribution.

The study clearly demonstrated the importance of gas-liquid interphase mass transfer particularly during the early stage of polymerization. A method of mass transfer correction was developed to obtain the true polymerization rate data as a function of time. Ignoring this mass transfer limitation could lead to serious misinterpretation of the rate data.

An optimum in productivity was observed at an Al/Ti ratio of approximately 15. At early polymerization times, no optimum productivity was observed. Competitive adsorption for active sites fails to explain this. Also, an optimum in productivity was observed at approximately 50°C.

The isotactic index increased with increasing temperature and decreased with increasing Al/Ti ratio. However, a significant improvement in tacticity, with no associated decrease in productivity, was observed when using small amounts of TMPIP additive ($5 \leq \text{TMPIP}/\text{Ti} \leq 25$).

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