

Propene Polymerization with MgCl₂-Supported TiCl₄/Dioctylphthalate Catalyst. II. Effects of Polymerization Conditions on the Microstructure of Isotactic Polymer

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SYNOPSIS

Propene was polymerized over the MgCl₂-supported TiCl₄/dioctylphthalate catalyst in heptane. Polymer products obtained under different polymerization conditions were separated into isotactic and atactic polypropenes by the extraction of boiling *n*-heptane. The effects of polymerization time, cocatalyst type, cocatalyst/catalyst ratio, polymerization temperature, and external base/cocatalyst ratio on the isotactic triad of the isotactic portion of polypropene were investigated. 2,2,6,6-Tetramethyl piperidine (TMPPI), dimethoxy diphenyl silane (DMDPS), and *t*-butylmethyl ether (TBME) were employed as the external Lewis base. High concentrations of the first two bases caused a decrease in isotactic triads in the isotactic polymer, while TBME showed no significant effects. The difference can be attributed to the different roles these external bases play in polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Heterogeneous Ziegler–Natta catalysts are known to polymerize propene (PP) into different stereospecificities. For example, MgCl₂-supported TiCl₄ catalysts with a combination of an aromatic diester and an alkoxy silane as internal and external bases, respectively, produce polypropene of very high isotacticity.^{1–4} The isotactic polymer therefore constitutes the major portion of polypropene products. The microstructure of the isotactic polymer can then be expected to have a significant influence on the polymer properties as a whole.

The microstructure of an isotactic polymer has been shown to be determined largely by the choice of a catalyst system,⁵ and is particularly important for the choice of an external Lewis base. For that reason, the effects of external base on catalyst activity and stereospecificity of MgCl₂-supported Ti catalysts have long been a focal point of numerous

research efforts. Their findings with respect to the roles of an external base can be briefly summarized as (1) selective poisoning of nonstereospecific sites,^{5–7} (2) conversion of nonstereospecific sites into stereospecific sites,^{1,5,8} (3) activating more stereospecific sites or enhancing propagation reaction rate,^{8–11} and (4) modifying stereospecific sites or transfer reaction.^{8–14} Those roles are not necessarily mutually exclusive.

Besides the choice of the catalyst system, polymerization conditions can also have significant influence on the microstructure of polymer chains. To the best of our knowledge, no detailed investigation has ever been done on this subject. In part I of this series,¹⁵ we discussed the effects of two different types of external bases on catalyst activity and polymer isotacticity. Here, the influence of polymerization conditions, including the use of three distinctly different types of external bases, on the stereospecificity of polymerization sites was studied. The changes in the microstructures of the whole polymer products, as well as the isotactic and atactic polymer portions of polypropenes, were examined. A two-isospecific-site model was used as the basis for data interpretation.

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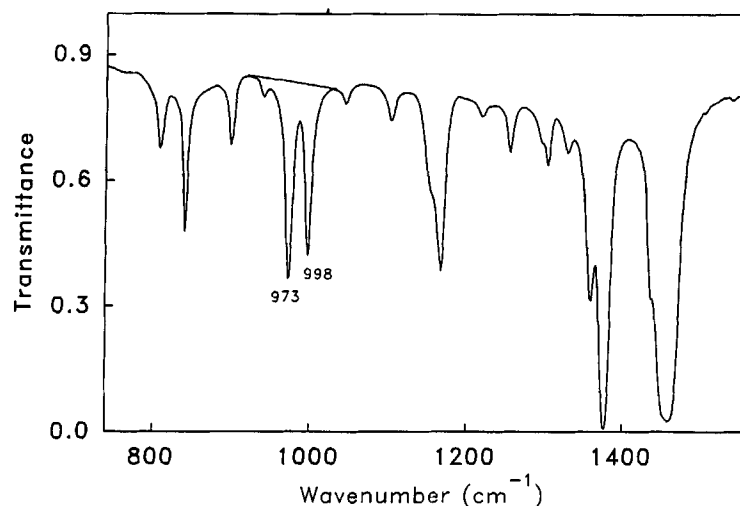


Figure 1 A typical IR spectrum of the isotactic polypropylene obtained with catalyst A in the 1560 cm^{-1} to 740 cm^{-1} region, showing the positioning of baseline. Polymerization conditions: $[\text{Ti}] = 0.12\text{ mmol/L}$; $\text{TEA/Ti} = 50$; temperature = 50°C ; propylene partial pressure = 118 kPa .

EXPERIMENTAL

The catalyst system chosen for the study was the MgCl_2 -supported TiCl_4 catalyst using dioctylphthalate (DOP) as the internal Lewis base. A detailed description for the preparation of three catalysts A, B, and C and for the polymerization procedure were given in part I of the series.¹⁵ The distinction among these three catalysts is the reaction temperature at which TiCl_4 was treated with MgCl_2 support to give different levels of phthaloyl chloride in the catalyst. The reaction temperatures were 85 , 95 , and 105°C for the catalysts designated A, B, and C, respectively. The phthaloyl level was the highest at 105°C .

The polypropylenes obtained using these catalysts were separated into two portions with the one insoluble in boiling heptane being designated as the isotactic polymer. For some isotactic PP samples, the microstructure was measured with ^{13}C -NMR (Bruker CXP-200 NMR spectrometer) at 120°C . Sample solutions for the NMR analysis were prepared as $10\text{ wt/vol } \%$ solution in *o*-dichlorobenzene at 120°C . The NMR was operated with 0.82 s of acquisition time and at a 45° pulse angle. Diglyme-*d*¹³ was used as an internal reference for chemical shifts, which is 57.7 ppm relative to tetramethyl silane (TMS). The spectra were baseline corrected. For the estimation of peak areas of methyl carbon region, the data were curve-fitted using a NMR 286 program (Chemistry Department, Queen's University, Kingston) and a modified version of PC116.¹⁶

The Lorentzian line shape function was used for the fitting.¹⁷

For infrared (IR) measurements, the isotactic PP samples were prepared according to Burfield and Loi.¹⁸ The sample films were pressed for about 5 s , removed from the press, and allowed to air-cool to room temperature. Before IR measurements, the samples were annealed for at least 7 days at room temperature. The spectra were obtained with a Bomem MB120 FTIR. For each polymer sample, at least three independently prepared films were measured. The baseline was drawn as shown in Figure 1 without baseline adjustment. The peak, at 998 cm^{-1} , was used as a measure of isotactic helix content, whereas the 973 cm^{-1} peak was taken as a reference. The IR absorbance bands at 998 cm^{-1} and 973 cm^{-1} have been linked to the appearance of the critical sequence length of $11\text{--}12$ and 5 monomer units, respectively.¹⁹ The advantage for using the absorbance band at 973 cm^{-1} as the reference band was reported to be "its sensitivity to low levels of isotactic units and its apparent insensitivity to thermal history effects."¹⁸ IR absorbance ratios, A_{998}/A_{973} obtained for each sample were converted to isotactic triad values using the following relationship, according to Burfield and Loi¹⁸:

$$A_{998}/A_{973} = 1.08[\text{mm}] - 0.15$$

where $[\text{mm}]$ is the isotactic triad.

From replicated measurements, the experimental error for $[\text{mm}]$ was estimated to be $\pm 0.3\%$ at 95% confidence level.

RESULTS AND DISCUSSION

Based on the procedure discussed in the previous section, the isotactic triads [mm] of isotactic polymers obtained under various polymerization conditions were estimated from their IR spectra, and the results are presented in Figures 2-5. The accuracy of the isotactic triad estimated from IR was cross-checked with ^{13}C -NMR spectroscopy. The difference between these two methods ranged from 0.3 to 1.4%.

^{13}C -NMR data also gave the pentad distributions of polymer samples (as presented in Table I) for the isotactic polypropenes obtained at six different polymerization temperatures. As indicated by the data, the isotactic pentad [mmmm], as expected, decreases with increasing polymerization temperature. All the isotactic polymers contain considerable chain defects, such as [rmmr], [rmrr], and [rrrm]. The effects of the external bases and polymerization processes on the isotactic pentad were not examined in this work. However, Busico et al.²⁰ found that the microstructure of the isotactic fractions of polypropenes remained fairly constant, showing only [mmmr], [mrrm], and [mrrm] defects under the influence of different external bases with or without an internal base. On the other hand, Paukkeri et al.²¹ analyzed PPs obtained under different polymerization processes to show that even the high molecular weight fraction of the PP produced by a slurry process contained some [rrrr] syndiotactic sequences, along with small amounts of [mmmr], [rmmr], [mrrm], and [mrrm].

Figure 2 shows a similar decreasing trend of the triad in the isotactic polymers with increasing temperature, as determined by the IR spectroscopy.

For MgCl_2 -supported TiCl_4 catalysts, many authors^{2,5} supported the idea of the coexistence of two different isospecific sites: (1) "low" isospecific sites featuring a Cl-vacancy that produce polymers

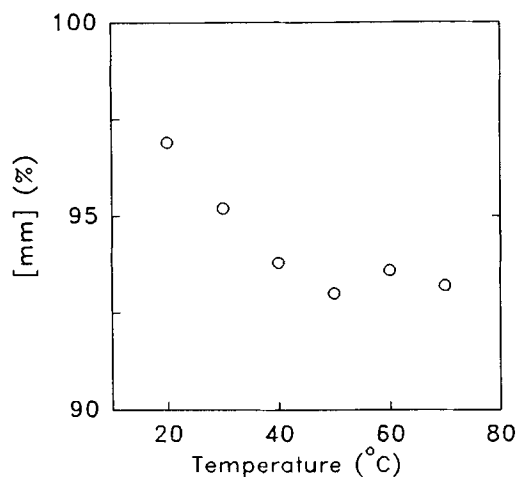


Figure 2 Effect of polymerization temperature on the fraction of the isotactic triad, [mm] in the isotactic polypropene estimated from IR spectra. Polymerization conditions were the same as in Figure 1.

of low isotacticity, and (2) "high" isospecific sites with a Lewis base attached that give a highly isotactic polymer. It is known that the internal Lewis base could be leached out into the polymerization medium by aluminum alkyl during polymerization.^{22,23} The effectiveness of the leaching process increases with temperature. Thus, it is understandable that isotactic triads decrease with increasing temperature. This is also consistent with the decrease in the isotactic index of the whole polymer with increasing temperature, as discussed in part I of this series.¹⁵

Table II presents the influence of various aluminum alkyls on the isotactic triads of the isotactic portion of the polymer. For all three catalysts prepared at 85, 95, and 105°C, the bulkiness of the alkyl group in the cocatalyst from ethyl to unbranched octyl shows a negative effect on the isotactic triad. This negative effect is likely a result of a rather

Table I Effect of Polymerization Temperature on Pentad Distributions of Isotactic Polypropenes Estimated from ^{13}C -NMR Spectroscopy

Temperature (°C)	mmmm	mmmr	rmmr	mmrr	mrrm + rmrr	rmm	rrrr	rrrm	mrrm
20	93.51	2.40	0.41	2.28	0.08	0.00	0.00	0.22	1.11
30	92.52	2.44	0.50	2.31	0.77	0.00	0.00	0.36	1.09
40	89.12	3.25	1.05	3.02	1.16	0.00	0.00	0.90	1.51
50	88.70	3.46	1.70	2.96	0.91	0.06	0.00	0.53	1.67
60	88.10	3.61	0.72	3.41	1.32	0.08	0.00	0.96	1.81
70	88.24	3.23	0.72	2.98	1.43	0.07	0.00	1.74	1.60

Polymerization conditions other than temperature were the same as in Figure 1.

Table II Effect of Aluminum Alkyls on the Fraction of Isotactic Triads, [mm] of the Isotactic Polypropylenes

Cocatalyst ^a	[mm] (mol %) ^b		
	A	Catalyst B	C
TEA	93.0	92.6	92.1
TIBA	92.4	90.6	90.1
TnHA	91.3	90.2	89.1
TnOA	90.7	89.9	89.0
IPRA	No activity	90.9	92.1

Polymerization conditions were the same as in Figure 1.

^a TEA, triethylaluminum; TIBA, triisobutylaluminum; TnHA, tri-*n*-hexylaluminum; TnOA, tri-*n*-octylaluminum; IPRA, isoprenylaluminum.

^b Experimental error for [mm] measurements was estimated to be $\pm 0.3\%$ at 95% confidence interval.

complicated interaction between the catalyst and cocatalyst. Even though the exact roles of the cocatalyst have not been unequivocally established, it has been generally agreed that the cocatalyst is involved in reduction and alkylation of the Ti catalyst, extraction of the internal base, and, to a certain degree, catalyst modification. Although the effectiveness of removing the internal base by aluminum alkyl may diminish as the alkyl group becomes increasingly bulky, the alkylation of the Ti species to form isotactic sites may be adversely affected by steric factors around the isotactic sites, as discussed earlier. Consequently, the activation of structurally more demanding high-isospecific sites may become more difficult as the bulkiness of the alkyl group increases, which leads to a decrease in isotactic triads of the isotactic polymer, as shown in Table II.

Isotactic triads of the isotactic polymer are also affected by the concentration of aluminum alkyl. Figure 3 presents the influence of the Al/Ti ratio on the isotactic triads for catalyst A: the isotactic triads decrease slightly with increasing Al/Ti ratios. Both triethyl aluminum (TEA) and triisobutyl aluminum (TIBA) show a similar effect. As discussed in part I,¹⁵ the strong complexation of an internal base of a diester nature (such as DOP) with Ti species and/or $MgCl_2$ makes the extraction of the internal base less susceptible to the increasing Al concentration. The above explanation also seems to be supported by Figure 4, where only a slight decrease in isotactic triad with polymerization time was observed.

When an external base is used, it plays a major role in enhancing the isotacticity of the catalyst. Its

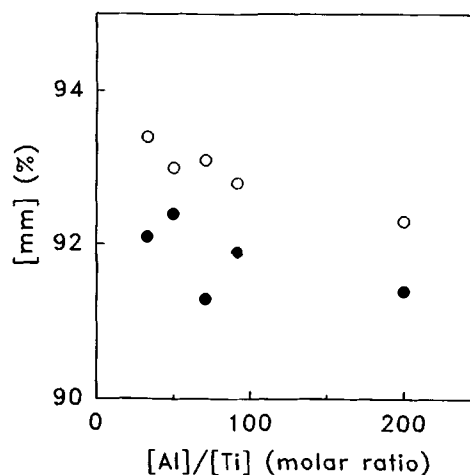


Figure 3 Effect of Al/Ti ratio on the isotactic triad of the isotactic polypropylene: O, triethylaluminum (TEA); ●, triisobutylaluminum (TIBA). Other polymerization conditions were the same as in Figure 1.

use also changes the microstructure of the isotactic polymer.^{5,13,14,24} The effectiveness of the external base in enhancing the isotacticity depends on the type and concentration of the external base for a given catalyst. In part I of this series,¹⁵ the influence of 2,2,6,6-tetramethyl piperidine (TMPiP) and dimethoxydiphenyl silane (DMDPS) on isotactic index was discussed. The major role of TMPiP and DMDPS was suggested to be the transformation of atactic sites to isotactic sites. The converted sites are believed to be the "high" isotactic sites, from the point of view that the presence of an external base increases the probability of sites being asso-

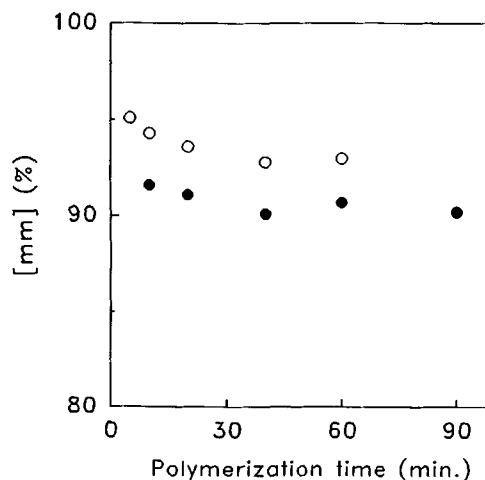


Figure 4 Effect of polymerization time on the isotactic triad of the isotactic polypropylene: O, triethylaluminum (TEA); ●, tri-*n*-octylaluminum (TOA). Other polymerization conditions were the same as in Figure 1.

ciated with the base. In this study, the enhancement of isotacticity was examined using three different types of external bases, namely *t*-butylmethyl ether (TBME), DMDPS, and TMPPI. The results are tabulated in Table III. For the addition of the external base, TMPPI, the isotactic triad of the isotactic polymer increased over that of polymerizations without an external base (Table II) by almost the same percentage for all three catalysts, regardless of whether the cocatalyst was TEA or TIBA. This suggests that the interaction between TMPPI and the cocatalyst is not important in determining the stereospecificity of the isotactic sites. On the other hand, for DMDPS, the enhancement of the isotactic triad of the isotactic polymer is greater for the isotactic polymer obtained with TEA cocatalyst than with TIBA, indicating that the interaction between cocatalyst and base plays a significant role in regulating the stereospecificity of the isotactic sites. A similar result was found for the alkoxy silane base.²⁵ For TBME, the effect of the base on the isotactic triad is not conclusive, although the isotactic triad seems to increase with the TEA cocatalyst.

The apparent difference in the effect of different external bases on the isotactic triad of the isotactic polymer prompted us to investigate this matter more closely by varying the concentration of the external base. First, the isotactic triads of the isotactic polymers obtained with different DMDPS/TEA (or TMPPI/TEA) ratios were examined, and the results are plotted in Figure 5. In both cases, the isotactic triads increased with increasing TMPPI/TEA or DMDPS/TEA ratio up to 0.05 and then decreased. In part I¹⁵ we discussed the fact that the

Table III Effects of External Bases on the Fraction of Isotactic Triads, [mm] of the Isotactic Polypropenes

Cocatalyst	External ^a Base	[mm] (%) ^b		
		A	B	C
TEA	TBME	94.9	95.3	92.5
	DMDPS	97.4	97.2	95.7
	TMPPI	96.5	95.0	94.6
TIBA	TBME	92.0	89.3	89.4
	DMDPS	93.8	92.8	92.7
	TMPPI	94.6	94.5	93.7

Polymerization conditions other than external base/Al ratio were the same as in Figure 1 (external base/Al = 0.05).

^a TBME = tri-*t*-butylmethyl ether; DMDPS = dimethoxydiphenylsilane; TMPPI = 2,2,6,6-tetramethylpiperidine.

^b See Table II for notation.

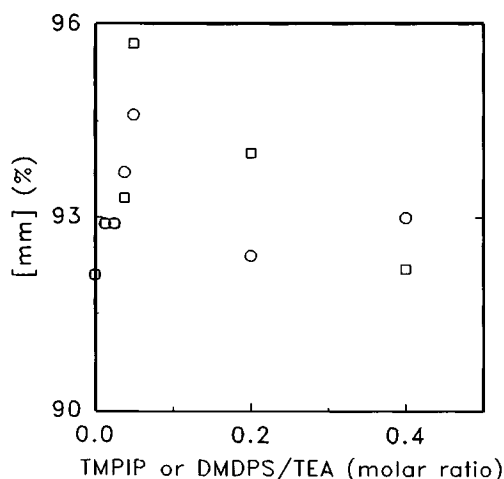


Figure 5 Effect of TMPPI or DMDPS/TEA ratio on the isotactic triad of the isotactic polypropene obtained with catalyst C: ○, TMPPI; □, DMDPS. Other polymerization conditions were the same as in Figure 1.

isotactic indices of the whole polymers also showed a maximum at the TMPPI/TEA or DMDPS/TEA ratio of 0.05. These results can be better explained using a structural model proposed previously by Kakugo et al.⁵ When the concentration of the external base is low, the external base can convert the aspecific sites into the high isospecific sites by complexing with one of the two vacancies at the aspecific sites. As the concentration of the external base increases, poisoning of not only the low isospecific sites but also the high isospecific sites takes place. An optimum ratio of external/cocatalyst, therefore, exists, at which the isotactic triads of the isotactic polymer display a maximum. The proposed mechanism is schematically shown in Figure 6.

In our previous publications,²⁶ we examined the effect of TBME on polymerization. When TBME was used as an external base, it enhanced the activity without affecting the isotacticity of the polymer for all three catalysts examined. The major role of TBME is to activate more catalytic sites, which is different from that of TMPPI or DMDPS. Figure 7 displays how the isotactic triad of the isotactic polymer varies with TBME/TEA ratios. TBME shows no apparent effect on [mm] at low TBME/TEA ratios, but [mm] increases at higher ratios. No maximum [mm] was observed, distinguished from what we have seen in the cases of TMPPI and DMDPS.

CONCLUSIONS

The microstructure of the isotactic fraction of polypropenes polymerized with the MgCl₂-supported

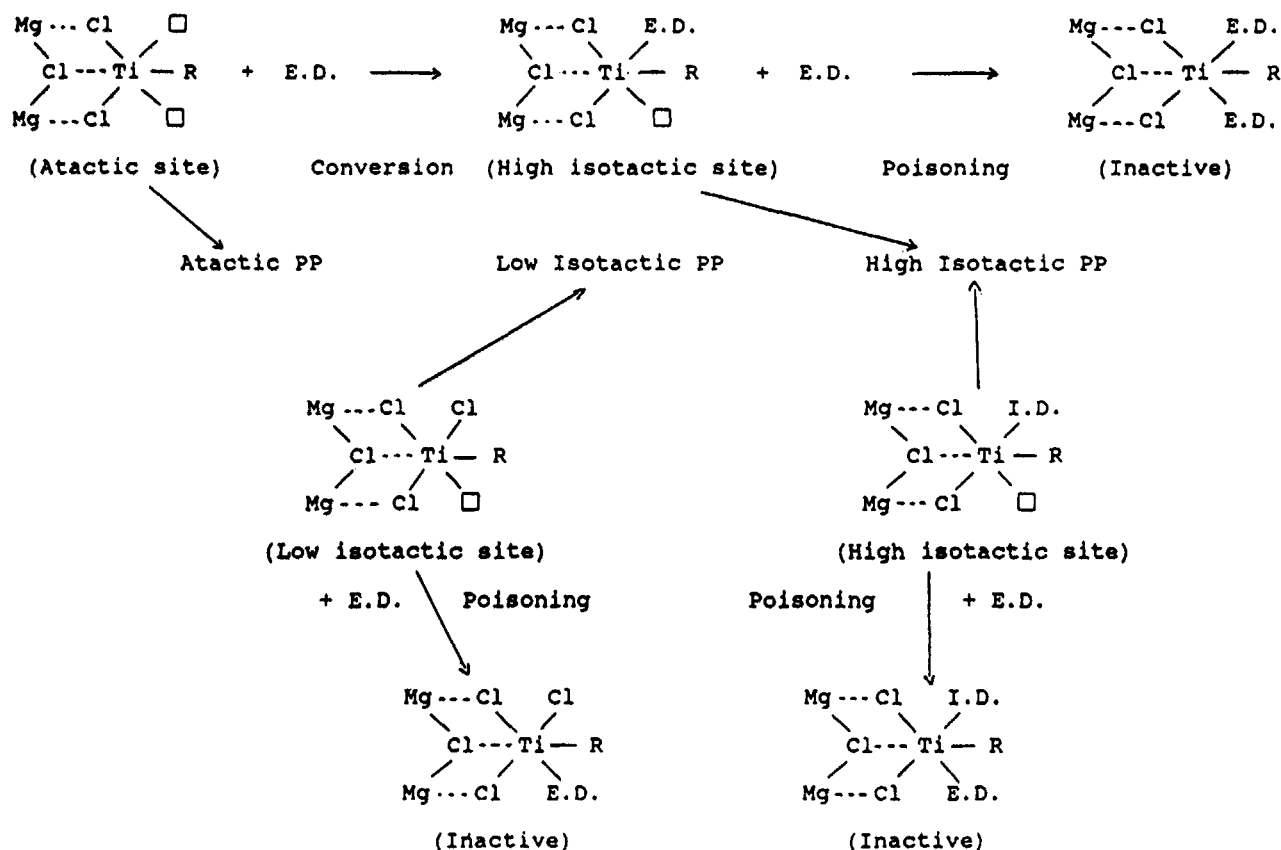


Figure 6 A proposed model for the possible transformations of active sites on the $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ catalyst under the influence of an external base.

TiCl_4/DOP catalyst is significantly affected by polymerization conditions. ^{13}C -NMR spectra show decreasing pentad from 93.5 to 88.2% as the polymerization temperature increases from 20 to 70°C. All

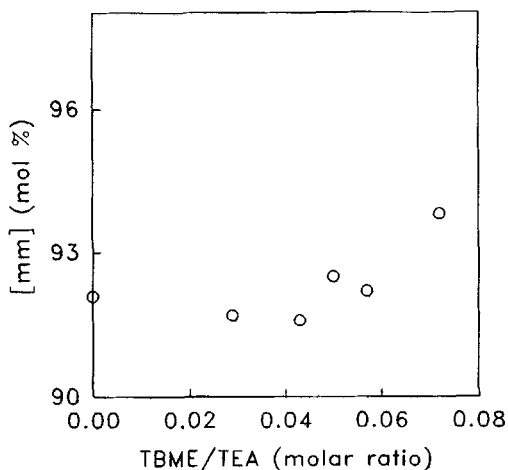


Figure 7 Effect of TBME/TEA ratio on the isotactic triad of isotactic polypropene obtained with catalyst C. Polymerization conditions were the same as in Figure 1.

the isotactic polypropenes contain considerable chain defects. The isotactic triad decreases as the alkyl group of the cocatalyst becomes increasing bulky. Due to the strong complexation of DOP as an internal base with active sites, the concentration of aluminum alkyl does not have an appreciable effect on the isotactic triad.

For the three different types of external bases examined, TBME seems to activate more potential sites; this, in turn, enhances catalyst activity but with little influence on isotacticity, at least at low concentrations of TBME. On the other hand, the transformation of aspecific into isospecific sites seems to be the major role of TMP/IP or DMDPS as an external base to enhance the isotacticity of polypropenes.

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