

Crystallinity and Isotactic Index of Polypropylene Samples Prepared by VOCl_3 and Aluminum Alkyls

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SYNOPSIS

The X-ray crystallinity and the isotactic index [II(%)] values were measured for polypropylene (PP) samples prepared by VOCl_3 and various aluminum alkyls. The reaction parameters, such as aging time, temperature, reaction medium, and additives, have some effect on the crystallinity of the samples. Among the three systems studied, a combination of $\text{VOCl}_3 + \text{Et}_2\text{AlCl}$ was found to give PP with higher crystallinity and II. In general, the tacticity of the samples prepared were much lower than the samples prepared with α -, β -, γ - TiCl_3 as the catalyst.

INTRODUCTION

The method of polymerization, catalyst system, solvent, and additives govern the properties of polyolefins. The use of crystalline TiCl_3 with aluminum alkyls for the olefin polymerization is well documented.¹ Polypropylene (PP) prepared with the above catalyst system mostly yields crystalline and isotactic product.^{2,3} The crystallinities and the isotactic index (II) of the PP samples prepared using VOCl_3 with Et_3Al , Et_2AlCl , and $\text{Al}(i\text{-Pr})_3$ are reported in this work. The influence of the various reaction parameters such as aging time of the catalyst, polymerization temperature, reaction medium, and additives on the crystallinity and II were studied.

EXPERIMENTAL

VOCl_3 was synthesized from V_2O_5 and SOCl_2 following the reported procedure.⁴ TEAL and DEAC were obtained as 20% solution in Versol from Polyolefin Ind. Ltd. (Bombay); concentration of these alkyls was determined iodometrically.⁵ *n*-Hexane, all other solvents, and additives used were of AR grade (from BDH Chemicals, Bombay) and purified following the reported procedures.⁶ Propylene gas

was obtained from BOC (U.K.) and argon was obtained from IOL, Bombay (India).

The samples for the X-ray diffraction (XRD) studies were compression molded at room temperature under a pressure of 3–4 atm in a stainless steel die. The samples for the Fourier transform infrared (FTIR) studies were compression molded as thin films at room temperature between steel plates. Since the moldings are at room temperature and under low pressure, there is no structural change occurring that can cause a change in the crystallinity. Hence the polymer is termed "as polymerized." The XRD of the samples were recorded on a Phillips PW1729 model with a PW1820 diffractometer and a copper target. The diffractograms of the PP samples in the form of pellets (thickness, 1.0–2.0 mm) were recorded from 5° to 40° (2θ values). Natta's method, as described by Weidinger and Hermans⁷ was used to calculate the crystallinity of the PP samples.

The FTIR spectra of the thin PP sample films were recorded on a Nicolet SX170 model. The II was derived from the absorbance ratio of the IR spectral bands at 995 and 973 cm^{-1} as reported by Luongo.^{8,9}

RESULTS AND DISCUSSION

XRD (Crystallinity, X_c , %)

For all the samples, irrespective of the catalyst system used, four distinct peaks were observed. A typ-

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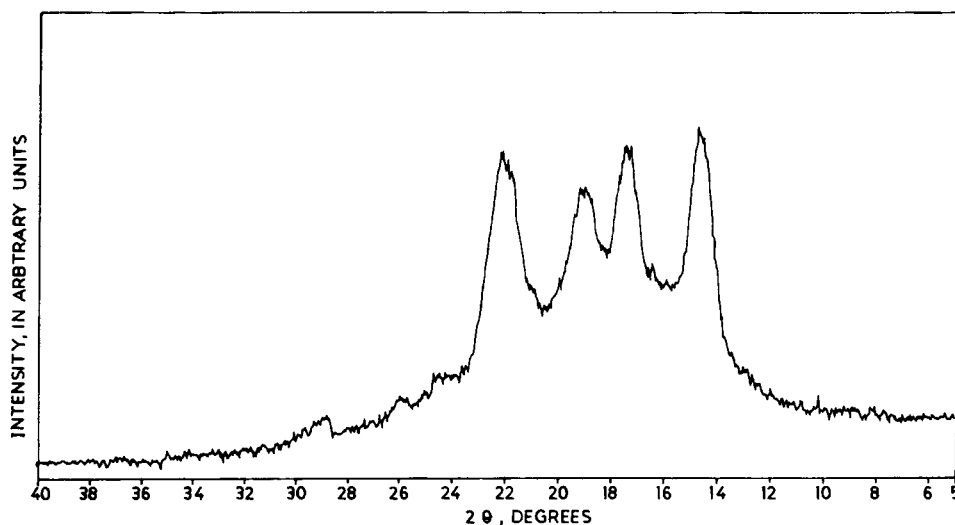


Figure 1 A typical X-ray diffractogram of PP sample prepared by VOCl_3 + aluminum alkyl.

ical X-ray diffractogram is given in Figure 1. From the reported diffractograms for *iso*-PP and *syn*-PP,^{10,11} it was seen that the peak positions (2θ values) were comparable to that reported for *iso*-PP. Details of the results obtained are summarized in Tables I to IV.

From Table I it can be seen that the three systems show the same trend, i.e., crystallinity improves slightly with aging time of the catalyst (optimum time is 40 min). However, samples prepared with VOCl_3 + Et_2AlCl system were more crystalline. The order of crystallinity observed was, VOCl_3 + Et_2AlCl > Et_3Al > $\text{Al}(i\text{-Pr})_3$. From the crystallinity data it can be seen that the samples obtained at higher aging time (60 min) are less crystalline. Probably at higher aging time the nature of the complex formed by catalyst and co-catalyst deteriorates and is least capable of regulating the incoming monomer in an ordered fashion.

Certain additives were found to improve the crystallinity of the polymer samples. Data is given in Table II. It may be possible that these additives react with both the catalyst components and in the process coordinate to less specific sites present on the complex surface and thus bring about more specificity.

As the polymerization temperature increases from 30 to 50°C, an increase in the crystallinity of the samples is observed (Table III). It may be possible that with increase of temperature some of the recessive reaction sites get activated and may help in better orientation of the polymer chain. Natta and co-workers have reported a similar kind of result with VCl_3 and Et_3Al and Et_2AlCl catalyst system.¹² However, from 50 to 55°C there is a decrease in the crystallinity. This may indicate that the catalyst is not very stable above 50°C.

For all the three catalyst systems, aliphatic sol-

Table I Effect of Aging Time on Crystallinity^a

Sr. No.	Aging Time (min)	Crystallinity (%)		
		$\text{Et}_3\text{Al} + \text{VOCl}_3$	$\text{Et}_2\text{AlCl} + \text{VOCl}_3$	$\text{Al}(i\text{-Pr})_3 + \text{VOCl}_3$
1	5	30.4	34.5	—
2	10	32.2	36.8	30.8
3	30	35.0	38.3	33.2
4	40	37.8	39.5	—
5	60	30.1	33.0	30.4

^a Reaction conditions: Reaction medium and temperature are *n*-hexane and 303 K, respectively (unless otherwise stated); reaction time = 90 min, flow rate = 50 mL/min.

Table II Effect of Additives on Crystallinity^a

Sr. No.	Additive	Crystallinity (%)		
		Et ₃ Al + VOCl ₃	Et ₂ AlCl + VOCl ₃	Al(<i>i</i> -Pr) ₃ + VOCl ₃
1	None	32.2	36.8	30.8
2	Et ₃ N	38.8	40.4	37.8
3	Hexamine	31.0	32.4	—
4	(<i>i</i> -Pr) ₂ ether	33.6	35.9	34.7
5	CHCl ₃	31.7	36.2	33.1
6	CCl ₄	—	—	30.2

^a Aging time = 10 min and other reaction conditions are the same as in Table I; additive = 0.125 mL.

Table III Effect of Temperature on Crystallinity^a

Sr. No.	Temperature (K)	Crystallinity (%)		
		Et ₃ Al + VOCl ₃	Et ₂ AlCl + VOCl ₃	Al(<i>i</i> -Pr) ₃ + VOCl ₃
1	303	32.2	36.8	30.8
2	313	36.7	38.0	33.6
3	323	37.6	39.6	34.2
4	328	32.5	34.1	28.0

^a Solvent = 30 mL (*n*-hexane); aging time = 10 min; reaction time = 90 min; and flow rate of propylene gas = 50 mL/min.

vents were found to be better than the aromatic ones (Table IV). We feel that the aromatic solvents may be interacting with catalyst components producing some adverse polymerization sites that may probably be causing some hindrance to an ordered orientation.

FTIR [Isotactic Index, II (%)]

A typical IR spectrum is shown in Figure 2. In general, it has been reported that products obtained with VOCl₃ systems have a low stereoregularity compared

to TiCl₃ systems.¹³ Tables V to VIII summarize the II data for PP samples prepared by the three catalyst systems.

It can be seen that isotactic index increases slightly with the aging time (Table V). This increase was more pronounced in the case of PP samples prepared by Et₂AlCl + VOCl₃ catalyst system. This may be probably due to the presence of relatively larger number of long-living sites capable of producing more isotactic polymer as compared to the other two catalyst systems.

Like crystallinity, II was also found to improve

Table IV Effect of Solvents on Crystallinity^a

Sr. No.	Solvent	Crystallinity (%)		
		Et ₃ Al + VOCl ₃	Et ₂ AlCl + VOCl ₃	Al(<i>i</i> -Pr) ₃ + VOCl ₃
1	<i>n</i> -Hexane	32.2	36.8	30.8
2	Cyclohexane	31.1	35.6	28.1
3	Benzene	29.2	34.0	26.6
4	Toluene	24.6	—	31.0
5	Chlorobenzene	30.9	34.9	29.4

^a Aging time = 10 min; reaction time = 90 min; and flow rate of propylene gas = 50 mL/min.

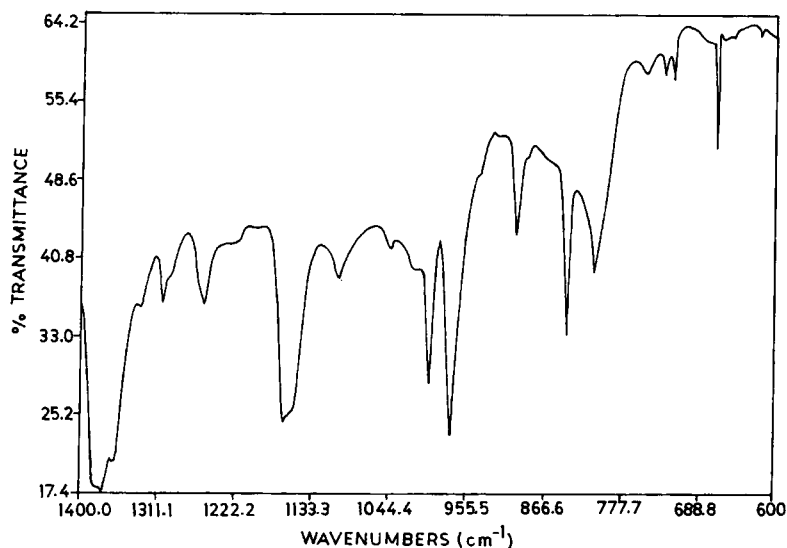


Figure 2 A typical FTIR spectra of PP sample (in the form of a film) prepared using VOCl_3 + aluminum alkyl at 30°C .

in the presence of certain additives (Table VI). The isotactic material obtained when VOCl_3 is used as a catalyst is reported to be 32% as compared to 80–

92% when $\alpha\text{-TiCl}_3$ is used,¹⁴ hence, for all three catalyst systems a considerable increase in II is noticed. Chlorine in Et_2AlCl seems to enhance the stereo

Table V Effect of Aging Time on Isotactic Index^a

Sr. No.	Aging Time (min)	Isotactic Index [II (%)]		
		$\text{Et}_3\text{Al} + \text{VOCl}_3$	$\text{Et}_2\text{AlCl} + \text{VOCl}_3$	$\text{Al}(i\text{-Pr})_3 + \text{VOCl}_3$
1	5	33.0	36.0	—
2	10	36.2	38.0	31.0
3	20	37.1	—	33.0
4	30	38.5	40.6	35.9
5	60	36.4	39.0	29.1

^a Reaction conditions are same as in Table I.

Table VI Effect of Additives on Isotactic Index^a

Sr. No.	Additive	Isotactic Index [II (%)]		
		$\text{Et}_3\text{Al} + \text{VOCl}_3$	$\text{Et}_2\text{AlCl} + \text{VOCl}_3$	$\text{Al}(i\text{-Pr})_3 + \text{VOCl}_3$
1	None	36.2	38.0	31.0
2	Et_3N	42.0	44.0	36.0
3	Hexamine	39.0	41.0	33.0
4	$(i\text{-Pr})_2$ ether	35.0	39.0	37.0
5	CHCl_3	30.0	30.0	32.0
6	CCL_4	—	—	28.0

^a Reaction conditions are same as in Table I, and aging time = 10 min; additive = 0.125 mL.

Table VII Effect of Temperature on Isotactic Index^a

Sr. No.	Temperature (K)	Isotactic Index [II (%)]		
		Et ₃ Al + VOCl ₃	Et ₂ AlCl + VOCl ₃	Al(<i>i</i> -Pr) ₃ + VOCl ₃
1	303	36.2	38.0	31.0
2	313	38.0	40.0	33.0
3	323	40.0	43.0	34.0
4	328	34.0	37.0	29.0

^a Reaction conditions are same as in Table I and aging time = 10 min.

specificity compared to Et₃Al and Al(*i*-Pr)₃. The additives may be complexing with the aspecific centers, converting them into isospecific ones. This behavior of additives has been reported by Boor.¹⁵ Recently, the role of certain additives in polymerization and its mechanism has been reported.¹⁶

The isotactic index of the samples prepared at various temperatures is given in Table VII. For all the three catalyst systems, a similar trend was noticed up to 50°C. However, by a 5°C increase in polymerization temperature, i.e., from 50 to 55°C, there is a decrease in the isotactic content. Hence it is found that 50°C is the optimum temperature for the polymerization of propylene using our catalyst system. It has been reported by Kissin that the average degree of stereo regularity is rather low and it slowly decreases as temperature increases for VOCl₃ and Al(*i*-Bu)₃ systems.¹⁷ It may be possible that in our systems temperature not only affects polymerization but also the structure of the catalytically active species.

The effect of various solvents on II is given in Table VIII. It can be seen that for all three systems more isotactic materials were obtained when ali-

phatic solvents were used as the reaction medium (same observation as for crystallinity).

CONCLUSIONS

From a comparative study of the X-ray crystallinity and isotactic index from IR spectra of as-polymerized PP samples the following conclusions can be drawn:

1. Similar trend was observed for both II and crystallinity values.
2. VOCl₃ + aluminum alkyls were found to give products of lower crystallinity and II as compared to the products obtained with TiCl₃ and aluminum alkyls.
3. Among the three catalyst systems studied, a combination of Et₂AlCl + VOCl₃ was found to give a product of higher crystallinity and II.
4. Crystallinity was found to increase with the increase in aging time up to 40 min. At higher aging time (i.e., 60 min), the complex formed

Table VIII Effect of Solvents on Isotactic Index^a

Sr. No.	Solvent	Isotactic Index [II (%)]		
		Et ₃ Al + VOCl ₃	Et ₂ AlCl + VOCl ₃	Al(<i>i</i> -Pr) ₃ + VOCl ₃
1	<i>n</i> -Hexane	36.2	38.0	31.0
2	<i>n</i> -Heptane	34.0	31.0	32.0
3	Cyclohexane	34.0	31.0	29.0
4	Benzene	38.0	30.0	28.0
5	Toluene	40.0	27.0	27.0
6	Chlorobenzene	—	—	29.0

^a Reaction conditions are same as in Table I and aging time = 10 min.

between the catalyst and co-catalyst deteriorates and is least capable of regulating the incoming monomer in an ordered fashion and hence crystallinity decreases.

5. The slight increase in II with aging time may be attributed to the fact that, at higher aging time, a few long-living sites capable of producing isotactic polymer may be present.
6. Certain additives were found to increase the crystallinity and II of the PP samples.
7. It was noticed that both crystallinity and II were higher in aliphatic solvents as compared to the aromatic solvents. There may be a possibility of aromatic solvents interacting with the catalyst components producing some adverse polymerization sites that may be causing some hindrance to an ordered orientation.

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