PII: S0032-3861(96)00986-X

Polymer Vol. 38 No. 17, pp. 4499–4503, 1997

0032-3861/97/$17.00+0.00

Polymerization of 4-methyl-1,3-pentadiene with MAO/Ti(OnBu)$_4$. The influence of preparation/ageing temperature upon the stereospecificity of the catalyst

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(Received 31 July 1996; revised 29 October 1996)

4-Methyl-1,3-pentadiene has been polymerized with the system Ti(OnBu)$_4$/MAO at different temperatures in the range +20°C to −78°C, using aged and unaged catalysts. The polymers obtained have a 1,2 syndiotactic or a mixed 1,2 syndiotactic/1,2 isotactic structure, depending on the polymerization temperature and on the temperature and time of ageing of the catalyst. The percentage of syndiotactic polymer depends on the polymerization temperature, but also on the time and temperature of ageing of the catalysts. The formation of isotactic polymer together with syndiotactic polymer has been attributed to the presence of two different active centres. The centres that produce the syndiotactic polymer increase with the time and temperature of ageing. © 1997 Elsevier Science Ltd.

(Keywords: titanium catalysts; polymerization; 4-methyl-1,3-pentadiene)

INTRODUCTION

Much attention has been given in recent years to the polymerization catalysts derived from methylaluminoxane (MAO) and some soluble titanium compounds such as CpTiCl$_3$, CpTi(OR)$_3$, Ti(OR)$_4$ and Ti(CH$_2$Ph)$_4$[1–10]. The importance of these catalysts lies in the fact that they are among the most active and stereospecific for the polymerization of styrene to syndiotactic polymer.

However, these systems are also active for the polymerization of 1,3-dienes, and can polymerize monomers, such as (Z)-1,3-pentadiene and 4-methyl-1,3-pentadiene, that are not polymerized by other soluble catalysts[11–15].

We have recently examined the polymerization of 4-methyl-1,3-pentadiene (4MP) with MAO/CpTiCl$_3$ and MAO/CpTi(OnBu)$_3$[14,15]; these systems give a 1,2 syndiotactic polymer independently of the polymerization temperature (in the range +20 to −78°C). We have now examined the polymerization of 4MP with MAO/Ti(OnBu)$_4$ and have found that it gives a 1,2 syndiotactic polymer or a mixture of isotactic and syndiotactic polymer, depending on the polymerization temperature and the ageing of the catalyst. This paper reports the results of this work.

EXPERIMENTAL

Materials

Ti(OnBu)$_4$ (Aldrich, 99% pure), CpTiCl$_3$ (Strem) and methylaluminoxane (MAO) (Witco, 30 wt% solution in toluene) were used without further purification. CpTi(OnBu)$_3$ was prepared according to the literature procedure[16]. Toluene (Fluka, >99.5% pure) and heptane (Fluka, >99.5% pure) were refluxed over Na for ca. 8 h, then distilled and stored over molecular sieves under dry nitrogen. 4-Methyl-1,3-pentadiene, prepared as reported in the literature[17,18], was refluxed for ca. 2 h over CaH$_2$, then distilled trap-to-trap and stored under dry nitrogen.

Polymerization

A standard procedure is reported. Monomer (2 ml) was introduced in a 50 ml dried glass reactor, toluene (16 ml) was then added and the solution was brought to the desired temperature. MAO (1×10^{-2} mol) and titanium compound (1×10^{-5} mol) were added in that order. When aged catalysts were used, the monomer was added at the end. The polymerization was terminated with methanol containing a small amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with fresh methanol, then dried *in vacuo* at room temperature.

Polymer characterization

Intrinsic viscosities were determined in toluene at 25°C using a Desreux–Bischof viscometer. ^{1}H and ^{13}C

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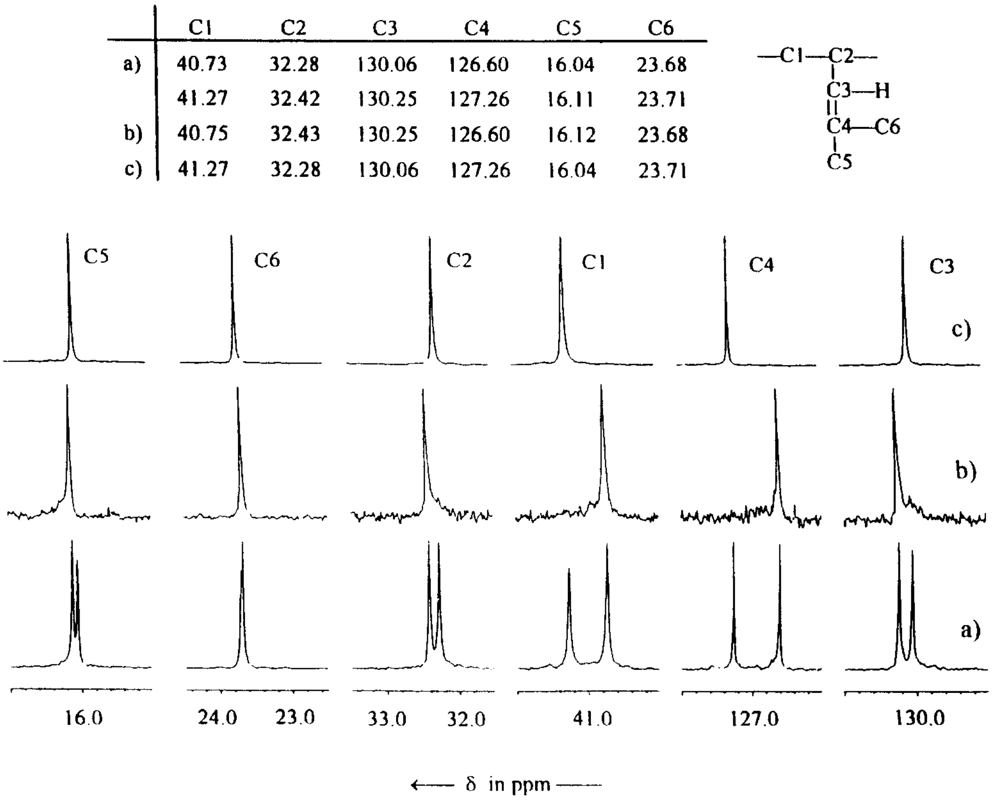
Table 1 Polymerization of 4-methyl-1,3-pentadiene with different Ti catalysts[a]

	Catalyst		Polymerization			1,2			
Exp.	Ti comp.	Moles × 10^5	Temp. (°C)	Time (min)	Conv. (%)	Iso (%)	Syndio (%)	M.p. (°C)	$[\eta]^b$ ($dl\,g^{-1}$)
1	$Ti(OnBu)_4$	0.5	20	26	92.8		≥99		0.6
2	$Ti(OnBu)_4$	0.5	0	40	32.6	25	75		
3	$Ti(OnBu)_4$	0.5	−18	330	100	41	59	96, 136	
4	$Ti(OnBu)_4$	0.5	−30	159	10.6	54	46	96, 146	2.7
5[c]	$Ti(OnBu)_4$	1	−30	1210	68.3		≥99	97	2.1
6[d]	$Ti(OnBu)_4$	0.5	−30	1800	100	50	50		2.5
7[e]	$Ti(OnBu)_4$	0.5	−30	320	12.7		100		
8[f]	$Ti(OnBu)_4$	0.5	−30	47 h	31.3	52	48		
9	$Ti(OnBu)_4$	4	−78	643 h	53.4	68	32		3.4
10[c]	$Ti(OnBu)_4$	4	−78	282 h	77.4		≥99		0.8
11[g]	$Ti(OnBu)_4$	1	+20	310	76.7		~100		
12	$CpTiCl_3$	0.44	20	4	100		~100		0.2
13	$CpTiCl_3$	0.44	−30	1.5	86.5		~100	98	0.8
14	$CpTiCl_3$	0.44	−78	55	21.6		~100	101	1.2
15	$CpTi(OnBu)_3$	0.5	20	1	75.3		~100		
16	$CpTi(OnBu)_3$	0.5	−30	1	42.3		~100		
17	$CpTi(OnBu)_3$	1	−78	125	20.2		~100		

[a] Polymerization conditions: monomer, 2 ml; toluene, 16 ml; MAO/Ti = 1000 (based on Al/Ti). Catalysts are used unaged, unless otherwise specified
[b] Determined in toluene at +25°C
[c] Catalyst aged for 30 min at room temperature
[d] Catalyst aged for 5 h at −30°C
[e] Catalyst aged for 45 days at −30°C
[f] Catalyst preformed and aged at −30°C for 5 h; only the filtered solution was used in the polymerization
[g] Heptane was used instead of toluene

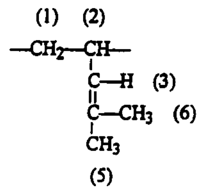


	C1	C2	C3	C4	C5	C6
a)	40.73	32.28	130.06	126.60	16.04	23.68
	41.27	32.42	130.25	127.26	16.11	23.71
b)	40.75	32.43	130.25	126.60	16.12	23.68
c)	41.27	32.28	130.06	127.26	16.04	23.71

Figure 1 67 MHz ^{13}C n.m.r. spectra ($C_2D_2Cl_4$, 110°C) of poly(4-methyl-1,3-pentadiene) obtained with (a) $Ti(OnBu)_4$/MAO at −30°C; (b) $TiCl_3$/$AlEt_3$ at +20°C; (c) $CpTiCl_3$/MAO at −30°C

n.m.r. examinations were performed with a Bruker AM270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 110°C (HMDS as internal standard) or in $CDCl_3$ at room temperature (TMS as internal standard). The concentration of the polymer solutions ranged from 3 to 10 wt%. D.s.c. scans were carried on a METTLER TA instrument. Typically, ca. 10 mg of polymer were analysed each run, and

	$CH_2(1)$	$CH(2)$	$CH(3)$	$CH_3(5)$	$CH_3(6)$
a)	0.81	2.13	4.75	1.46	1.64
	1.07		4.79	1.52	1.66
	1.17				
b)	1.07	2.14	4.75	1.46	1.66



$-CH_2-CH(-CH=C(CH_3)-CH_3)-$

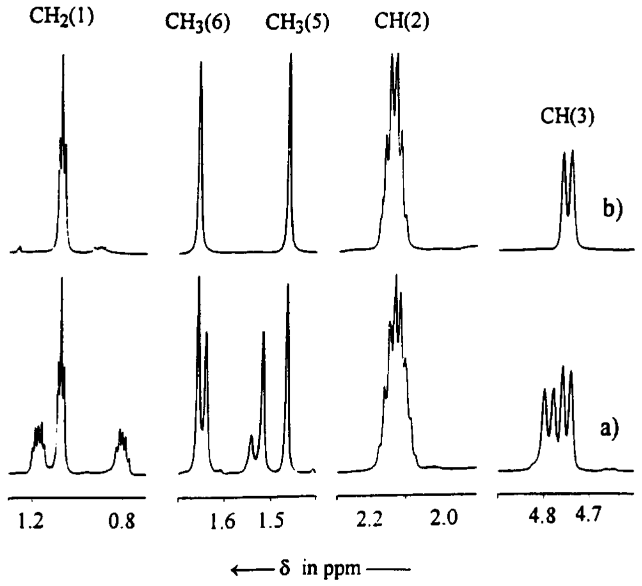


Figure 2 500 MHz ^1H n.m.r. spectra ($CDCl_3$, 25°C) of (a) poly(4-methyl-1,3-pentadiene) obtained with $Ti(OnBu)_4/MAO$ at −30°C; (b) poly(4-methyl-1,3-pentadiene) obtained with $CpTiCl_3/MAO$

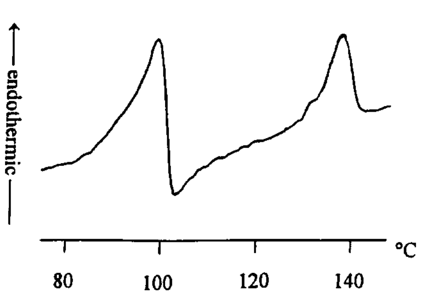


Figure 3 D.s.c. chromatogram of poly(4-methyl-1,3-pentadiene) obtained with $Ti(OnBu)_4/MAO$ at −18°C

the scan speed was ca. 20 K min^{-1} under nitrogen atmosphere.

RESULTS AND DISCUSSION

Table 1 reports some data on the polymerization of 4MP with the $MAO/Ti(OnBu)_4$ system. Some data on polymerization with the systems $CpTiCl_3/MAO$ and $CpTi(OnBu)_3/MAO$ are reported for comparison.

While the systems based on $CpTiCl_3$ and $CpTi(OnBu)_3$ give a 1,2 syndiotactic polymer, either at room temperature or at −78°C (*Table 1*, runs 12–17), $Ti(OnBu)_4/MAO$

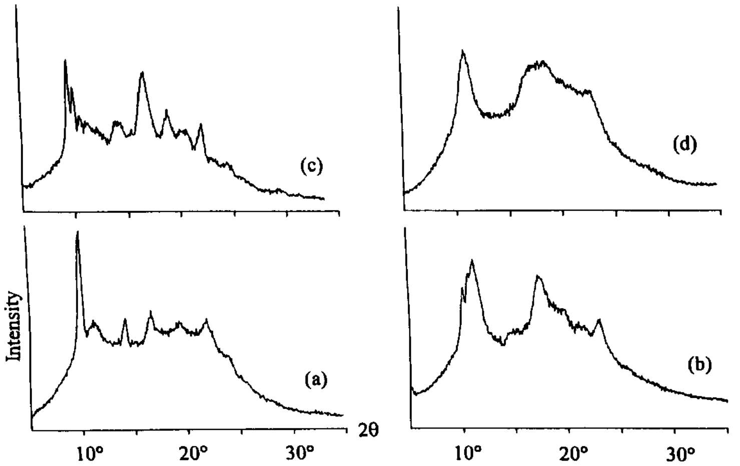


Figure 4 X-powder spectra of poly(4-methyl-1,3-pentadiene) obtained with (a) $CpTiCl_3/MAO$ at −30°C; (b) $TiCl_3/AlEt_3$, diethylether insoluble fraction; (c) $Ti(OnBu)_4/MAO$ at −30°C, crude polymer; (d) $Ti(OnBu)_4/MAO$ at −30°C, methylethylketone soluble fraction

gives a 1,2 syndiotactic polymer at room temperature (*Table 1*, run 1) and a mixture of isotactic and syndiotactic polymers at lower temperatures (*Table 1*, runs 2–4, 9).

Figure 1 shows the ^{13}C n.m.r. spectra of (a) poly(4MP) obtained at −30°C with $Ti(OnBu)_4/MAO$; (b) 1,2 isotactic poly(4MP) obtained at +20°C with the system $AlEt_3/TiCl_3$ (violet modification); the structure of this polymer was determined by X-ray analysis[19]; (c) 1,2 syndiotactic poly(4MP) obtained with $CpTiCl_3/MAO$ at −30°C. The spectrum of *Figure 1a* appears as the sum of the spectra of *Figures 1b* and *1c*.

The presence of both iso- and syndiotactic poly(4MP) in the product obtained with $Ti(OnBu)_4/MAO$ at low temperature is also evident from the ^1H n.m.r. spectrum (*Figure 2*), from the d.s.c. diagram (*Figure 3*), which shows two different melting points, and from the X-ray powder spectra (*Figure 4*), which exhibit the crystallinity of both the structures.

Attempts to separate the isotactic polymer from the syndiotactic one by extraction with different solvents were unsuccessful; both the polymers were present in all the fractions, although the syndiotactic polymer was predominant in the fractions extracted with low boiling solvents (acetone, diethylether) and the isotactic polymer in the fractions extracted with higher boiling solvents (2-butanone).

As reported in *Table 1*, the isotactic content increases with decreasing polymerization temperature, the amount of iso- and syndiotactic polymer being practically the same at −30°C.

The effect of ageing on the stereospecificity of the catalysts prepared at different temperatures was examined. Catalysts prepared and aged at room temperature for 30 min gave only 1,2 syndiotactic poly(4MP) in polymerizations carried out at −30°C or −78°C (*Table 1*, runs 5 and 10). Catalysts prepared and aged at −30°C for 5 h gave a mixture of isotactic and syndiotactic poly(4MP) (*Table 1*, run 6), while those aged at −30°C for 45 days gave only syndiotactic polymer (*Table 1*, run 7).

Work has also been carried out to examine whether the change of stereospecificity, from syndiotactic to isotactic, might be related to the formation of a heterogeneous phase at low temperature. Some sort of flocculant precipitate is usually observed in the catalysts prepared at −30°C, independently of the ageing time. The hypothesis that the isotactic polymer might derive from the heterogeneous portion of the catalyst is difficult to accept in view of the results obtained with catalysts aged at room temperature and used at −30°C or with catalysts prepared and aged for a long time at −30°C. These catalysts, in which a small amount of heterogeneous phase is present at low temperature, give syndiotactic poly(4MP) only.

In addition, when heptane was used as solvent instead of toluene (*Table 1*; run 11), no difference was observed in the structure of the polymer obtained, although the catalyst is less soluble in heptane than in toluene; in polymerizations of 4MP carried out with catalysts prepared and aged at −30°C for a few hours, the structure of the polymers was the same, whether using all the catalyst suspension or only the filtered solution.

All the above data seem to indicate that two active species form in the reaction of MAO with $Ti(OnBu)_4$. The species that gives the syndiotactic polymer increases with the time and temperature of ageing of the catalyst.

As a working hypothesis, we propose that the isotactic polymer derives from a Ti(IV) and the syndiotactic from a Ti(III) species. This hypothesis is in accord with the data of the literature concerning the reaction between aluminium alkyls and $Ti(OnBu)_4$, $CpTiCl_3$ and $CpTi(OnBu)_3$[8,20–23]. $CpTiCl_3$ and $CpTi(OnBu)_3$ are rapidly reduced by MAO to Ti(III)[8,23]; these compounds give catalysts that produce syndiotactic poly(4MP) only. The reaction between MAO and $Ti(OnBu)_4$ has not been studied, but it is known that $Al(iBu)_3$ reduces $Ti(OnBu)_4$ to Ti(III) only slowly, in reactions carried out at room temperature[20–22].

It is known that $MAO/Ti(OnBu)_4$ is an effective catalyst also for the polymerization of styrene[1,4,6]. We have examined the polymerization of this monomer with $MAO/Ti(OnBu)_4$ under the conditions that give, from 4MP, a mixture of iso- and syndiotactic polymer, but have obtained only syndiotactic polystyrene. It has been reported that the active species in the Ti catalysts used for the polymerization of styrene to syndiotactic polymer is Ti(III)[8,24]. Failure to obtain isotactic polystyrene with $MAO/Ti(OnBu)_4$ at −30°C may be attributable to the fact that the Ti(IV) species is inactive for the polymerization of styrene.

CONCLUSIONS

The system $MAO/Ti(OnBu)_4$ produces, from 4MP, a 1,2 syndiotactic polymer at room temperature, while products containing both isotactic and syndiotactic polymers are obtained at lower temperatures. Both these polymers are crystalline by X-ray analysis.

Ageing of the catalyst affects the composition of the products, in the sense that the ratio of syndiotactic to isotactic polymer increases as the reaction between MAO and $Ti(OnBu)_4$ proceeds. The results indicate that two different active centres are present in the system $MAO/Ti(OnBu)_4$.

Isotactic poly(4MP) has been obtained so far only with heterogeneous systems[19]. This work shows that it can also be obtained with soluble systems.

Polymerization of styrene with $MAO/Ti(OnBu)_4$ at low temperature gives syndiotactic polystyrene only. This is probably due to the fact that the species that gives isotactic poly(4MP) is inactive for styrene polymerization.

ACKNOWLEDGEMENT

We wish to thank Mr Giulio Zannoni and Mr Salvatore Italia for technical assistance.

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