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Stereoselective 1-3-butadiene polymerization using new titanium chelates

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ABSTRACT

Ternary titanium chelates $Ti_x(RCOO^-)_y(C_{16}H_{11}O_6^-)_z$ (R = H, CH_3, CH_3CH_2) combined with $AlEt_2Cl$ selectively polymerise 1,3-butadiene giving >95% cis-1-4-polybutadiene. The stereoselectivity, activity and oligomer contents are dependent on reaction temperature and Al/Ti ratio.

INTRODUCTION

The stereospecific Ziegler-Natta polymerization of butadiene in high cis-1,4-unit contents is of industrial interest due to the elastomeric properties of these polymers [1]. In the present paper we describe the use of three new ternary titanium chelates which in conjunction with $AlEt_2Cl$ catalyse the polymerization of butadiene to cis-1,4 polybutadienes in homogeneous medium. The effects of molar ratios Al/Ti, of temperature in the range 50° C to 100° C, and of reaction time have been examined with respect to oligomer and polymer molecular weight distributions. The influence of the nature of the ligands of Ti on polymer stereospecificity was also investigated.

EXPERIMENTAL

General procedures

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts were measured in ppm relative to TMS external standard. IR spectra were recorded on a Mattson 3020 FTIR spectrophotometer. Calorimetric experiments were carried out on a 12000 PL-DSC equipment and the catalytic reaction products were analyzed by gas chromatography on a HP 5890 chromatograph with FID detector, equipped with a polydimethylsiloxane column 30 m, 0.25 mm id, and film tickness of 0.2 μm, between 80°C and 180°C with a heating rate of 10°C/min. Elemental analyses were performed on a Perkin Elmer 2400 equipment.

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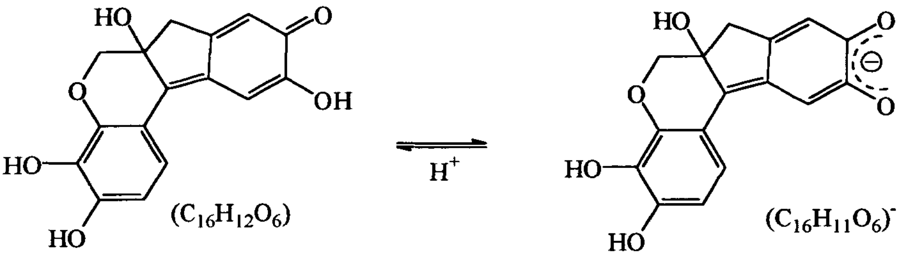
Preparation of Chelates

Carboxylic acids were distilled before use. Hemateine ($C_{16}H_{12}O_6$) (I) was prepared by controlled oxidation of hematoxylin according to literature (2).



I

Metallic Ti (28.7 mg, 0.6 mmol) and powdered I (120 mg, 0.4 mmol) were added to 40 mL of a 90% aqueous solution of formic acid. The mixture was refluxed for aproximately 30 hours. A dark blue powder was obtained. After centrifugation, the solid complex was washed 6 times with water and 6 with ethanol and finally dried in a vacuum dessicator over P_4O_{10}. 158 mg (0.13 mmol, 66%) of $[Ti_3(C_{16}H_{11}O_6)_2(HCOO)_{10}]$ were obtained The acetate and propionate derivates were prepared by analog procedures, giving the complexes $[Ti(C_{16}H_{11}O_6)_2(CH_3COO)_2]$ and $[Ti(C_{16}H_{11}O_6)_2(C_2H_5COO)_2]$ in 60% and 50 % yields, respectively, with 60 hours of reflux. All three compounds are insoluble in most of the common solvents.

Analytical Data of Complexes

$[Ti_3(C_{16}H_{11}O_6^-)_2(HCOO^-)_{10}]$ - IR (KBr pellets): 3400 cm^{-1} [vO-H, vs], 1625 cm^{-1} [vC=O, $HCOO^-$, m], 1570 cm^{-1} [vC=O, $C_{16}H_{11}O_6^-$, m]. Calc. for $C_{42}H_{32}O_{32}Ti_3$: C, 42.31; H, 2.71; N, 0.00 %. Found: C, 42.68; H, 2.89; N, 0.00 %.

$[Ti(C_{16}H_{11}O_6)_2(CH_3COO^-)_2]$ - IR (KBr pellets): 3400 cm^{-1} [vO-H, vs], 1630 cm^{-1} [vC=O, CH_3COO^-, m], 1580 cm^{-1} [vC=O, $C_{16}H_{11}O_6^-$, m]. Calc. for $C_{36}H_{28}O_{16}Ti$: C, 56.56; H, 3.69; N, 0.00 %. Found: C, 55.28; H, 3.87; N, 0.00 %.

$[Ti(C_{16}H_{11}O_6^-)_2(C_2H_5COO^-)_2]$ - IR (KBr pellets): 3400 cm^{-1} [vO-H, vs], 1630 cm^{-1} [v C=O, $C_2H_5COO^-$, m], 1580 cm^{-1} [vC=O, $C_{16}H_{11}O_6^-$, m]. Calc. for $C_{38}H_{32}O_{16}Ti$: C, 57.59; H, 4.07; N, 0.00 %. Found: C, 56.64; H, 4.62; N, 0.00 %.

Polymerization reactions

Toluene was distilled from sodium under argon before use and was handled and stored under inert atmosphere. $AlEt_2Cl$ was kept freeze-dried under dry argon.

Catalytic polymerizations were carried out in a glass flask in a 180 mL stainless steel autoclave. The powdered titanium chelate was introduced in the reactor under argon and

20 mL of toluene were injected into the autoclave. The reactor was cooled to -80°C under magnetic stirring, 10 mL of liquid 1,3-butadiene were introduced and the appropiate volume of $AlEt_2Cl$ solution was added. The reactor was closed and heated to the required temperature, keeping the system under stirring. After the reaction, the $AlEt_2Cl$ was destroyed by exposure to air. It is important to note that the titanium complexes are only soluble in the reaction medium in the presence of alkylalluminium and precipitate after this cocalyst is consumed.

Polymer characterisation

Antioxidant was added to the reaction. Polymer products were precipitated with methanol (2:1 V:V) and dried in vacuo. Conversions were calculated from the weight of isolated polymer compared to the initial monomer charge. *Cis* contents of the polymers were measured by IR spectroscopy (films) and ^1H NMR and ^{13}C NMR spectroscopies (in $CDCl_3$) according to known methods [3,4]. Molecular weights and molecular weight distributions of the polymers were determined by viscosity and gel permeation chromatography, using THF as solvent. Oligomer conversions were obtained by gas chromatography after polymer precipitation.

RESULTS AND DISCUSSION

All three $Ti_x(RCOO^-)_y(C_{16}H_{11}O_6^-)_z$ (R = H, CH_3, CH_3CH_2) complexes gave similar results, considering percent of conversion and stereoselectivity, under the same conditions; this indicates negligible influence of the R group. Table I contains the principal results obtained with $Ti_3(HCOO^-)_{10}(C_{16}H_{11}O_6^-)_2$. As is shown, polymerization is favoured at 50°C with higher [Al]/[Ti] ratio; the catalyst turnover is practically mantained when the chelate concentration is increased (entries 1 and 2). A higher catalytic activity was observed at 100°C, but also a higher yield in oligomers was produced (entry 3). Under similar conditions but with [Al]/[Ti] = 3, the activity of the system is diminished and the polymerization is slower (2-3% polymer; 9-11% oligomer), which is probably due to the lower acidity of the medium (entries 4 and 5).

Table 1- Polymerization data of 1,3-butadiene using $Ti_3(HCOO^-)_{10}(C_{16}H_{11}O_6^-)_2$ and $AlEt_2Cl$ in toluene.

Entry	T (°C)	t (h)	[Ti] (mmol)	Yield Oligomer (%)	 Polymer (%)	TO*
1	50	6	1.2	-	10	10.5
2	50	15	3.1	-	25	10.2
3	100	15	3.1	30	20	20.3
4	80	20	1.2	9	2	11.5
5	85	20	1.2	11	3	14.7

Conditions: [Al]/[Ti] = 10; 20 ml of toluene and 10 mL of 1,3-butadiene.

* Turnover = mol(product).mol(Ti)$^{-1}$.

IR, ^1H and ^{13}C NMR spectra of polymer obtained in entry 2 are shown in Figures 1 and 2. Figure 1 shows the high cis-isomer content of the polymer (band at 738 cm^{-1}). Accoording to Figure 2, it is possible to conclude that only the cis-isomer is detected (>95%) by ^{13}C NMR (peaks at 27,56 ppm and 129,6 ppm).

Molecular weight determination of sample 2 (entry 2) by GPC indicates: M_w=19260 Da and M_n=2710 Da, giving a broad polydispersity (M_w/M_n=7.1). Molecular weight determination by viscosity gives 13200 Da.

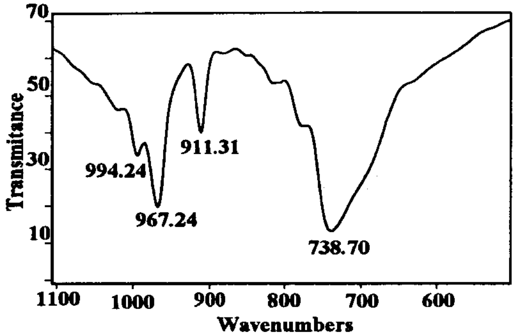


Figure 1 - IR spectra of polymer obtained in entry 2.

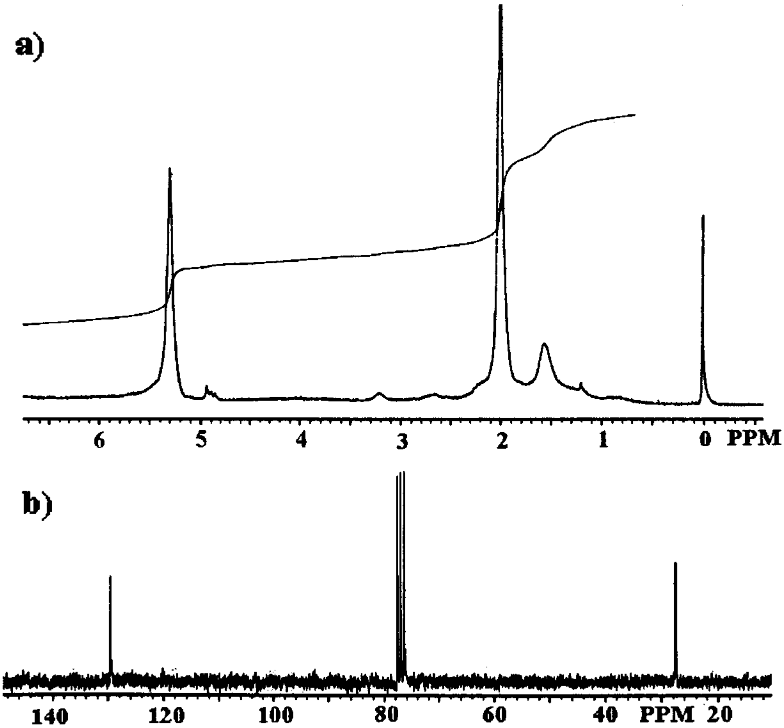


Figure 2 - (a) ^1H and (b) ^{13}C NMR spectra of polymer obtained in entry 2.

CONCLUSIONS

The ternary chelates $[Ti_x(RCOO^-)_y(C_{16}H_{11}O_6^-)_z]$ are good precursors for the stereospecific polymerization of 1,3-butadiene in conjuction with $AlEt_2Cl$ cocatalyst. All three chelates show similar performance. Maintaining the same ortohydroxyquinoid ligand but varying the carboxylate ion in the chelate, it was not possible to observe any change in the stereospecifity on polymer yield. It is thus probable that the good performance of the system is due mainly to the influence of the ortohydroxyquinoid ligand, in view of its good donor property [5] and considerable delocalisation of the pi-electron density of hemateine.

ACKNOWLEDGEMENTS

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