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Inversion of stereoselectivity in 1,3-butadiene polymerization with a niobium catalyst induced by a change in the solvent system

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Summary

Catalytic 1,3-butadiene polymerization systems can be obtained with the new complex $[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ as a catalyst. When the catalysis occurs in a homogeneous medium (toluene as a solvent) in conjunction with $AlEt_2Cl$, cis-1,4-polybutadiene is obtained. A remarkable inversion of stereoselectivity has been observed when the catalysis is carried out in a two phase system with the molten salt $AlCl_3$.1-methyl-3-n-butyl-imidazolium chloride (MBIC) as a solvent and $AlEt_2Cl$ as a cocatalyst, giving the trans 1,4-polybutadiene.

Introduction

The application of niobium compounds and materials as catalysts for various industrially useful reactions is becoming increasingly important in recent days (1). There are few reports for reactions catalyzed by some organometallic compounds of niobium in homogeneous medium but apparently there is no reference to a Nb soluble polymerization catalyst.

We recently reported the preparation of titanium-hemateine-carboxylate ternary complexes for the homogeneous polymerization of 1,3-butadiene to high cis-1,4 content. (2). Using the same chelating ligand (hemateine) we were able to synthesise a niobium soluble catalyst $[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ which associated with $AlEt_2Cl$ in toluene medium, can also polymerize 1,3-butadiene to high cis content polybutadiene (>95%). A remarkable inversion of stereoselectivity to the trans-1,4 mode has been observed when the same catalyst system was used in a chloroaluminate molten salt of the type $AlCl_3$.1-methyl-3-n-butylimidazolium chloride (MBIC).

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In recent years, two-phase systems for catalysis have been introduced with success (3,4) and now several of them have industrial applications (5-7). Carlin and Wilkes have used a chloroaluminate molten salt for the Ziegler-Natta polymerization of ethylene with Cp_2TiCl_2 as a catalyst (8). However, until now there has been no report on the application of Nb- catalysts in two-phase systems.

Room temperature molten salts based on aluminium (III) chloride and 1,3-dialkylimidazolium chloride (DAIC) proved to be specially suitable for that purpose. They are good solvents for inorganic salts but do not dissolve hydrocarbons (9). They have controlable Lewis acidity and donor/acceptor properties through a variation of the $AlCl_3$/DAIC molar ratio (or Al(III) molar fraction) in the medium (10-12). After the catalytic process the molten salt settles and the products in the upper phase are easily separated from the catalyst dissolved in the ionic medium. The catalyst performance, considering the stereoselectivity of the products can be modulated by adjusting the Lewis acidity of the system.

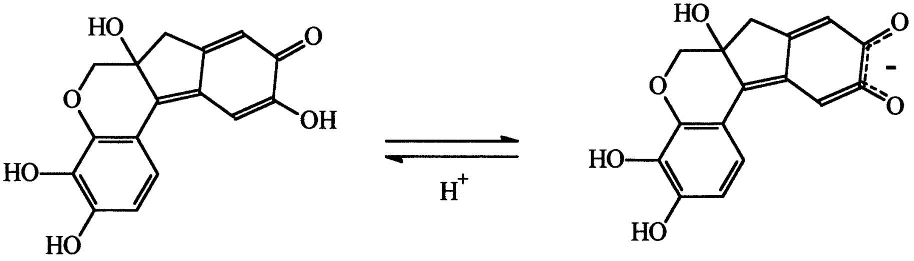
Experimental

General Procedures

Routine ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 Mz spectrometer at ambient temperature. Chemical shifts were referenced to TMS as an external standard. ^{13}C-NMR spectra of the polymer products were measured in $CDCl_3$. Infrared spectra were recorded on a Perkin Elmer PE 1430 spectrophotometer. Elemental analysis were performed on a Perkin Elmer 2400 equipment. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a Waters 150 equipment operating with a refraction index detector at room temperature.

Preparation of the catalyst

Acetic acid was distilled before use. Hemateine ($C_{16}H_{12}O_6$) was prepared by controlled oxydation of hematoxylin according to the literature (13):



I

In a typical procedure, 50 mg (0,11 mmol) of the complex $[NH_4.H_2NbO(C_2O_4^{2-})_3.3H_2O]$, (from C.B.M.M., Brazil) and 165 mg (0.55 mmol) of **I** were additioned to 100 mL of a 90% aqueous solution of acetic acid. The mixture was refluxed for 5 hours. A dark blue powder was obtained. After centrifugation, the solid complex was washed several times with water, ethanol and finally dried in a vacuum dessicator over P_4O_{10}. A yield of 60% in $[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ was obtained. The compound is insoluble in most of the common organic solvents and in water, but can be dissolved in the reaction medium in the presence of alkylaluminium compounds. It is also completely soluble in the molten salt when used in two-phase catalysis.

Analytical data of the complex.

$[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ - IR (KBr pellets) 3400 cm^{-1}[νO-H, vs ,$C_{16}H_{11}O_6^-$]; 1715 cm^{-1} [νC=O, vs, $C_2O_4^{2-}$]; 1576 cm^{-1} [νC=O, m, $C_{16}H_{11}O_6^-$]; 830 cm^{-1} [νNb=O,vs,] 450 cm^{-1} [νNb-O, m]. Calc. for $NbC_{18}H_{11}O_{11}$: C, 43.56; H, 2.22; N, 0.00%. Found: C, 43.65; H, 2.38; N, 0.00%.

Preparation of the molten salts.

The molten salts were prepared by published procedures (14). The Lewis acidity of this medium was adjusted by varying the molar fraction of Al (III) chloride (x) between 0,50 and 0,57, using also as a modulator of the acidity the cocatalyst $AlEt_2Cl$.

Polymerization reactions in homogeneous medium

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

Catalytic polymerizations were carried out in a 180 mL glass lined stainless steel autoclave. The niobium catalyst (0.04 mmol) was introduced in the reactor under argon and 20 mL of toluene were injected into the autoclave. The system was freezed to -80°C under magnetic stirring, 10 mL of liquid 1,3-butadiene were introduced, the appropiated volume of $AlEt_2Cl$ solution in toluene was added and the reactor was heated to the required temperature, under stirring. After the reaction the $AlEt_2Cl$ was destroyed by exposition to the air.

Polymerization reactions in molten salt

Polymerization was carried out in a 150 mL glass reactor. In the reactor were introduced the molten salt (3 mL), the niobium complex (0,025 mmol), the cocatalyst ($AlEt_2Cl$) in sufficient amount to obtain the desired Lewis acidity and butadiene (80 mmol). In all experiments the [Al]/[Nb] ratio was kept at a value of 10. The system was maintained under stirring in a thermostated circulation bath. During the experiments butadiene polymers were accumulated over the ionic melt, forming a two-phase system. All reactions were performed during 2 hours, when the products were separated from the ionic phase. In these conditions the conversion was constant (> 95%).

Characterization of Polymers.

After the reaction antioxidant was added to the medium. Polymer products were precipitated with methanol (2:1 V:V) and dried in vacuum. A very small amount (less than 1 %) of oligomer, dissolved in methanol, was obtained in each experiment. Conversions were calculated from the weight of isolated polymer compared to the initial monomer charge. The different stereoisomers of polymers were determined by IR spectroscopy (films) and ^1H and ^{13}C NMR spectroscopies (in $CDCl_3$) according to known methods (15,16). Molecular weights and molecular weight distribution were determined by viscosity and gel permeation chromatography (GPC) using THF as solvent.

Results and discussion

Table 1 shows the results of the catalytic performance of $[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ in the 1,3-butadiene polymerization using a two-phase medium. The Al (III) molar fraction (x) in the molten salt of the ionic phase, expressed as:

$$X_{A1} = [A1]/[A1] + [MBIC]$$

was varied from 0.50 to 0.57, increasing by this way the Lewis acidity of the system, in order to find out the optimum conditions for stereoselectivity. As can be concluded by the results in Table 1, the performance of the catalytic system is markedly dependent on the Lewis acidity of the medium and on the temperature.

Table 1 - Polymerization data of 1,3-butadiene using $[NbO(C_{16}H_{11}O_6^-)(C_2O_4^{2-})]$ and $AlEt_2Cl$ in two-phase systems.

Entry	Lewis acidity of ionic phase	T (°C)	Stereoselectivity (a) 1,4 - trans (b) 1,4 - cis (c) 1,2 - vinyl
1	0.50	-5	no reaction
2	0.51	-5	no reaction
3	0.54	50	(a), (b) and (c)
4	0.54	5	(a) and (c)
5	0.54	0	(a) >> (c)
6	0.54	-5	(a) (> 95%)
* 7	0.54	-30	no reaction
8	0.57	50	(a), (b) and (c)
** 9	0.54	-5	(a), (b) and (c)

* The liquid phase solidifies

** Control run in the absence of the Nb-catalyst. (Acid generalized catalysis)

When the acidity is low, i.e. $x_{Al} = 0.51$ (entry 2) no polymerization occurs. The best value of x_{Al} for stereospecificity control is 0.54. Whithin this acidity value we studied the influence of temperature. As can be seen, the stereospecificity in *trans PBD* increases rapidly below 0° C, being -5° C the best value. At -30° C (entry 7) the liquid phase solidifies and stops the catalytic activity. In basic melts ($X_{Al} < 0.50$) where the dominant ions are Cl^- and $AlCl_4^-$ (8) no catalytic activity is observed. This may be attributed to several factors including the lower activity of the Nb complex in the melts due to strong interaction with the Cl^- anions present. On the other hand, when the acidity of the melt is higher than 0,51, where the dominant anions are $Al_2Cl_7^-$ and $AlCl_4^-$ (8), the Nb complex is quite active. It appears that if the amount of these ions is insufficient no reaction is observed. Also if they are in great excess no stereoselectivity is obtained. One should also consider the bulky nature of the ligand (hemateine) of the Nb catalyst. It should represent a steric hindrance to the insertion of the substrate to the metal atom, making possible only or predominantly one type of stereoisomer.

An unusual inversion of stereoselectivity is observed changing from two-phase to homogeneous catalysis (toluene as a solvent). Working with the same Al/Nb ratio in both types of catalysis and also with the same Nb complex and cocatalyst $AlEt_2Cl$, temperature 50° C and 5 hours, *cis-1,4-polybutadiene* is obtained with stereospecificity higher than 95%, as can be concluded by the IR and ^{13}C-NMR spectra.

GPC of polymer obtained in entry 6 of Table 1 gives $M_w = 1.8$ kDa with polydispersion of 3.1. The polymer obtained in homogeneous medium gives by GPC $M_w = 105$ kDa with polydispersion of 1.5.

Conclusions

For the first time a soluble Nb-catalyst has been prepared which associated to $AlEt_2Cl$ can polymerize 1,3-butadiene to high specificity. When the polymerization is carried out in homogeneous medium (toluene as a solvent), cis-1,4 - polybutadiene is obtained (>95%). An inversion of stereoselectivity to the trans-1,4 mode (>95%) is obtained if the catalysis is carried out in a chloroaluminate molten salt of the type $AlCl_3$.1-methyl-3-n-butylimidazolium chloride.

The stereospecificity of the Nb-catalyst appears to be related mainly to the ortohydroxyquinoid ligand of the complex molecule in view of its good donor property (17) and considerable delocalisation of the pi-electron density of hemateine. Similar behavior has been also observed with Ti-hemateine-carboxylate complexes (2). On the other hand, the unusual inversion of stereoselectivity is apparently related to the bulky nature of the hemateine ligand and to the dominant chloroaluminate anions ($AlCl_4^-$, $Al_2Cl_7^-$) in the Lewis acidic medium.

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