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Co- and terpolymerizations of α-olefins and dienes with MgH_2-supported Ziegler catalyst

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ABSTRACT

Copolymerizations of ethylene or propylene with butadiene, 1,5-hexadiene or 1,7-octadiene by $MgH_2/TiCl_4$-$AlEt_3$ catalyst system were carried out. The effect of diene concentration in the reaction medium for each polymerization system on catalytic activity was observed. The compositions of the obtained copolymers were evaluated and the reactivity ratios were determined. Ethylene-propylene-diene terpolymerizations with the same catalyst system were also investigated.

INTRODUCTION

The copolymerizations of olefins and dienes in spite of their practical interest have been little studied. The copolymers having low contents of dienes present high molecular weights and high crystallinity of polyolefin type. These copolymers can be used either for conventional vulcanization with sulfur or for other chemical modifications1). Recently some papers dealing with the polymerization of butadiene2,3), 1,5-hexadiene4,5), 1,7-octadiene6) and the copolymerization with α-olefins have been published.

This paper presents the results of co- and terpolymerization of ethylene, propylene and the dienes cited above using $MgH_2/TiCl_4$-$AlEt_3$ Ziegler catalyst, that was previously employed in the ethylene homopolymerization and copolymerization with higher α-olefins7,8).

EXPERIMENTAL PART

Materials

Toluene, 1,5-hexadiene and 1,7-octadiene, were stirred over Na/K-alloy and distilled under argon. Triethylaluminium (TEA) and $TiCl_4$ were used after distillation. Argon was used after passage through a molecular sieve 3 Å column. Butadiene was passed through a molecular sieve 3 Å column and condensed before use. Ethylene and propylene were used after passing through a molecular sieve 3 Å column.

Catalyst synthesis

The $MgH_2/TiCl_4$ catalyst was prepared by the procedure described in an earlier paper7).

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Polymerization procedure

All polymerizations were carried out in a 250 ml glass reactor (Buechi, Uster) with toluene as solvent. The catalyst suspension and the comonomers were put into the reactor. For the copolymerization systems the α-olefin was introduced under appropriate pressure (ethylene: 0.7 bar and propylene: 2.0 bar). The polymerization was initiated by injecting TEA into the reaction mixture. The olefin was continously fed and its polymerization rate was followed by a flowmeter. In the terpolymerizations propylene was charged to the reactor (2.0 bar) and ethylene (excess pressure of 0.7 bar) was then continously fed. The reactions were stopped by the addition of methanol.

Analytical procedures

IR spectra from polymer films were obtained with a Nicolet Fourier transform spectrometer. The composition of the polymers were estimated by IR spectroscopy or through the area under the trace produced by the flowmeter and the weight of the obtained polymer.

RESULTS AND DISCUSSION

Homopolymerization of the diene mononers were carried out with the $MgH_2/TiCl_4\text{-}AlEt_3$ catalyst system. The order of reactivity was found to be:

1,3-Bd > 1,5-Hd >> 1,7-Od.

(Bd=Butadiene; Hd=Hexadiene; Od=Octadiene).

Figures 1 and 2 show respectively the effect of comonomer addition in ethylene-diene and propylene-diene copolymerizations.

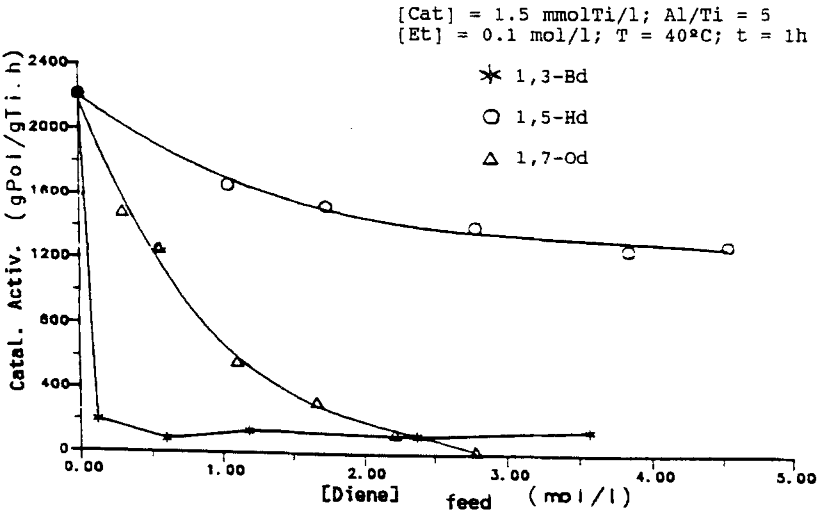

Figure 1
Influence of diene concentration in the feed on catalyst activity (Ethylene-Diene)

As can be seen the introduction of a low amount of butadiene caused a drastic decrease of catalyst activity, which tended to grow as the diene concentration increased. This behaviour was attributed to the stronger coordination of the conjugated diene with the active centers. In the case of 1,5-Hd the results showed that its copolymerization with ethylene did not much affect catalyst activity. In fact this diene is even more active than propylene. As expected, the larger 1,7-Od was a stronger inhibitor than 1,5-Hd.

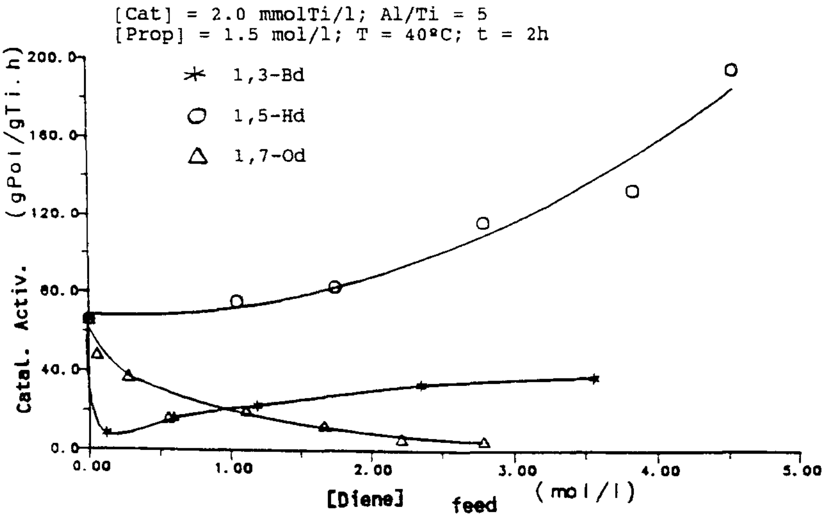

Figure 2
Influence of diene concentration in the feed on catalyst activity (Propylene-Diene)

Figures 3 and 4 show the copolymer compositions at different diene concentrations for ethylene-diene and propylene-diene copolymerizations. The amount of diene incorporated in ethylene copolymers increased to almost the same level for 1,3-Bd and 1,5-Hd but much less for 1,7-Od. In the propylene-1,3-Bd copolymerization the results showed that the polymer produced practically did not incorporate propylene. Propylene-1,5-Hd copolymers in all compositions ranges were obtained and the proportion of 1,7-Od in propylene copolymers were higher than in ethylene copolymers.

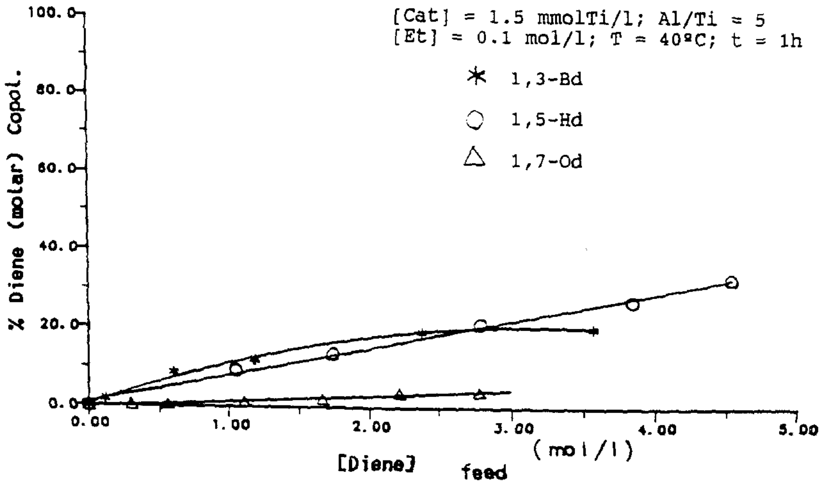

Figure 3
Influence of diene concentration in the feed on copolymer composition (Ethylene-Diene)

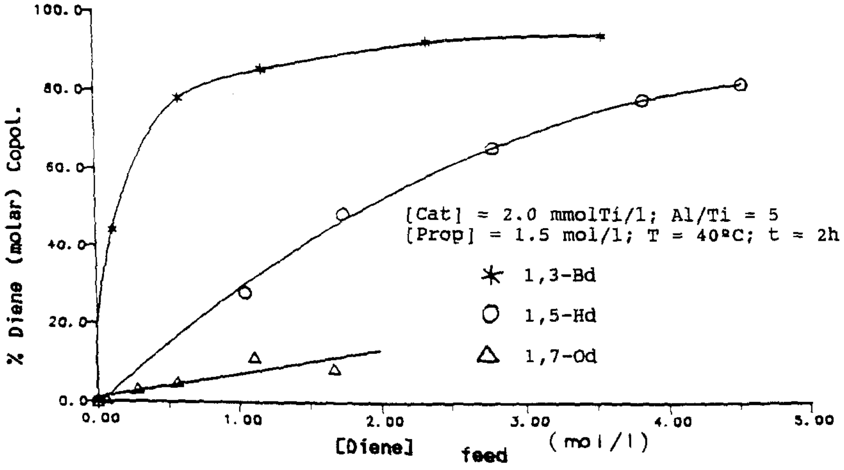

Figure 4
Influence of diene concentration in the feed on copolymer composition (Propylene-Diene)

Tables 1a and 1b present reactivity ratios for the systems studied, calculated by the Fineman-Ross method.

Ethylene (r_1); diene (r_2)

Diene	r_1	r_2	$r_1 \cdot r_2$
1,3-Bd	67.3	0	0
1,5-Hd	105.4	11.10^{-3}	1,1
1,7-Od	1049	25.10^{-3}	26

(a)

Propylene (r_1); diene (r_2)

Diene	r_1	r_2	$r_1 \cdot r_2$
1,3-Bd	0,08	7,4	0.6
1,5-Hd	6,5	4.4	28,6
1,7-Od	5,1	0	0

(b)

Table 1
Reactivity ratios for ethylene-diene (a) and propylene-diene (b) copolymerizations

The results of ethylene-propylene-diene terpolymerizations are represented in Figures 5 and 6. The same behaviour in relation to catalyst activity was observed with 1,3-Bd as termonomer. The behaviour observed with 1,5-Hd in the terpolymerizations seems to be the sum of both copolymerization effects on the catalyst activity (Figures 1 and 2). The inhibition effect of 1,7-Od was smaller than that in ethylene copolymerization.

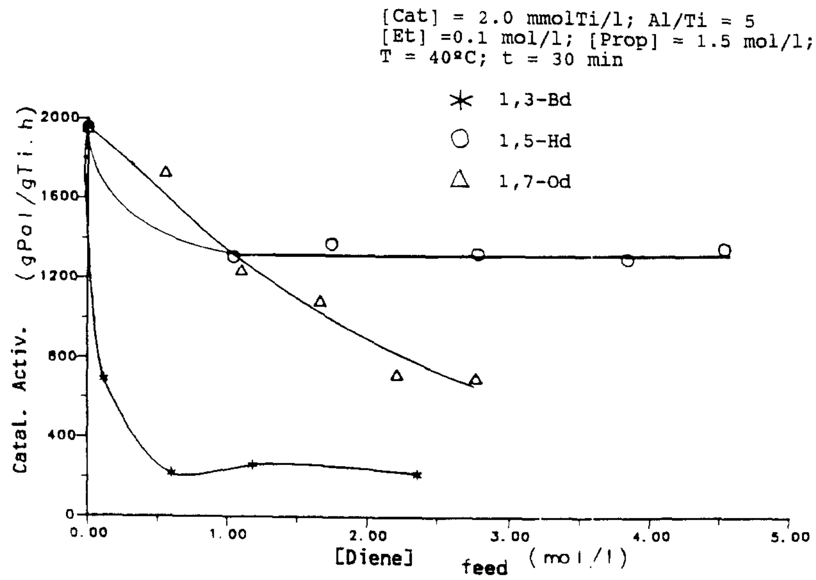

Figure 5
Influence of diene concentration in the feed on catalyst activity (E-P-D terpolymer)

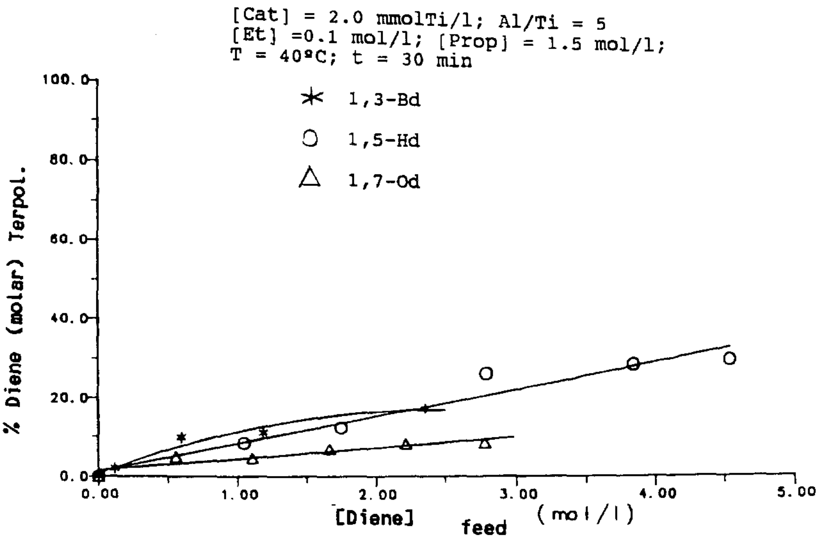

Figure 6
Influence of diene concentration in the feed on diene content in the polymer (E-P-D terpolymer)

The contents of ethylene and propylene incorporated in all terpolymers were plotted against diene concentration (Figure 7). It can be seen that the higher the diene content, the lower the propylene content in the terpolymer; the ethylene content in the terpolymers did not show significant variation.

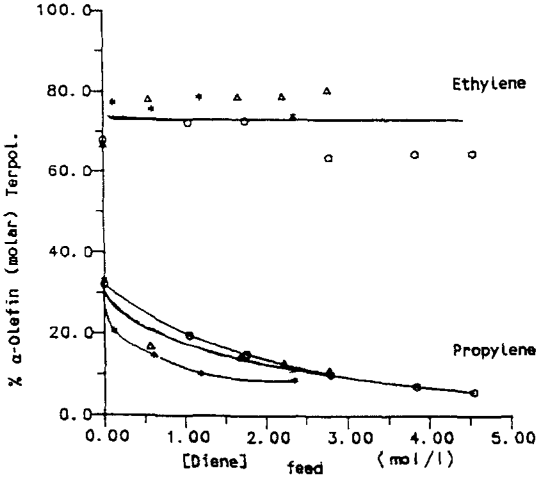

Figure 7
Influence of diene concentration in the feed on α-olefin incorporated in the terpolymer

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