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Synthesis of ethylene-propylene-diene terpolymers with supported Ziegler-Natta catalyst

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ABSTRACT

Terpolymerizations of ethylene, propylene and diene (1,3-butadiene, 1,5-hexadiene or 1,7-octadiene) by $MgH_2/TiCl_4$-$AlEt_3$ catalyst system were carried out. The compositions of the obtained terpolymers were evaluated. The effect of diene concentration in the reaction medium for each polymerization system on the terpolymer composition was observed. The structure of the diene repeat units was also investigated.

INTRODUCTION

EPDM elastomers exhibit high chemical resistance because of the virtual absence of double bonds in the main chain. The third monomer (2-3%) provides unsaturated sites along the backbone, which improve cross-linking response with peroxides and permit direct sulfur cure[1]. The most used catalyst for this particular terpolymerization is based on vanadium compounds. However, highly active catalysts of titanium chloride supported on magnesium compounds have been developed and intensively studied for α-olefins homo- and copolymerizations[2,3].

The preliminary results of α-olefin-diene co- and terpolymerizations using the $MgH_2/TiCl_4$-$AlEt_3$ catalyst system were previously reported[4]. The influence of termonomer concentration on catalyst activity for ethylene-propylene-diene terpolymerizations was verified.

In the present paper, the behaviour of the above mentioned terpolymerizations with the MgH_2-supported catalyst is reported. 1,3-Butadiene (1,3-Bd), 1,5-hexadiene (1,5-Hd) and 1,7-octadiene (1,7-Od) were the termonomers used in this study. Recently these dienes have received special attention because they are considerably simpler than those employed in the industrial processes for the same purpose[5,6].

EXPERIMENTAL PART

Materials

Toluene, 1,5-hexadiene (1,5-Hd) and 1,7-octadiene (1,7-Od), 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. 1,3-Butadiene (1,3-Bd) was passed through a molecular sieve (3 Å) column and condensed

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before use. Ethylene (Et) and propylene (Prop) were used after passing through a molecular sieve (3 Å) column.

Catalyst synthesis

$MgH_2/TiCl_4$ catalyst was prepared by the procedure described in the literature[7].

Polymerization procedure

All terpolymerizations were carried out in a 250 ml glass reactor (Buechi, Uster) with toluene as solvent. The catalyst suspension and the termonomer (liquid 1,3-butadiene, 1,5-hexadiene or 1,7-octadiene) were put into the reactor; propylene was introduced until the pressure of 2.0 bar and ethylene to an excess pressure of 0.7 bar. The reaction temperature was 40ºC. Then the polymerization was initiated by injecting TEA into the reaction mixture. Ethylene was continously fed and its polymerization rate was followed by a flowmeter. 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 curve produced by the flowmeter and the weight of the obtained polymer.

RESULTS AND DISCUSSION

For all terpolymerizations the mole ratio of ethylene/propylene was stated at 1/15 in the reaction mixture and the concentration of diene was varied.

Ethylene-propylene-1,3-butadiene terpolymers

Table 1 presents the results obtained for the terpolymerizations[8]. The influence of 1,3-butadiene concentration in the reaction mixture (between 0.12 and 2.36 mol/l) on polymerization rate (Figure 1) shows the strong inhibition of the catalyst by this diene. The same effect was already mentioned in the literature[9].

Reation #	[1,3-Bd] (mol/l)	Catalyst Activity (pPol/gTi.h)	Et (%mol)	Prop (%mol)	1,3-Bd (%mol)
EP-03	0	1954	66.8	33.2	0
EPB-01	0.12	692	77.3	20.7	2.0
EPB-02	0.60	218	75.6	14.7	9.8
EPB-03	1.19	261	78.7	10.4	10.9
EPB-04	2.36	216	74.0	8.9	17.1
HBd	-	-	0	0	100

Table 1
Results of ethylene-propylene-1,3-Butadiene terpolymerizations[8]

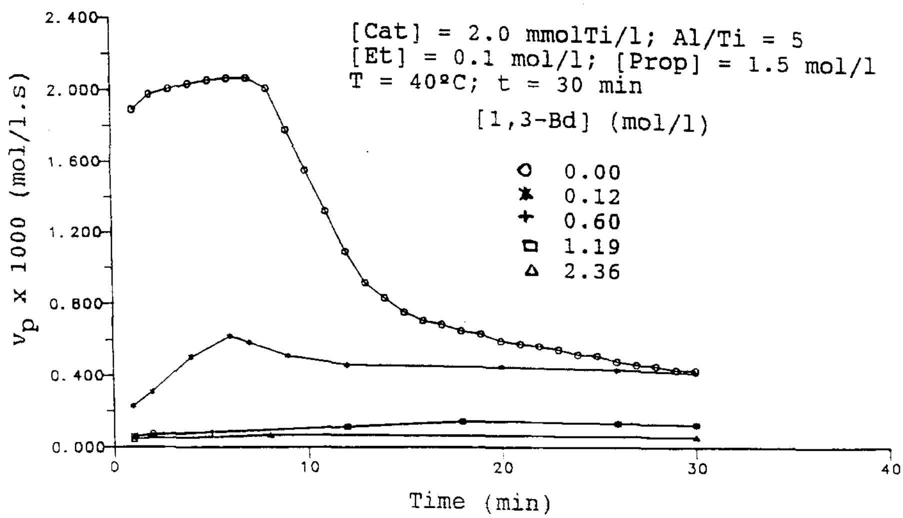

Figure 1
Influence of diene concentration on the rate of ethylene-propylene-1,3-butadiene terpolymerization[8)]

Figure 2 shows the effect of diene concentration in the medium on the contents of the three components in the terpolymer chains. Although ethylene content did not change in the studied range, the propylene content decreased as 1,3-butadiene amount increased.

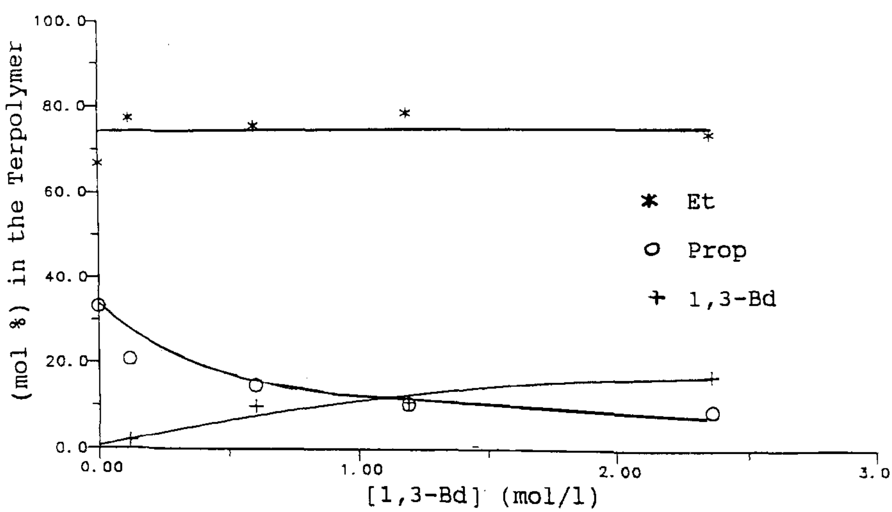

Figure 2
Influence of 1,3-Bd concentration on polymer composition

The distribution of 1,3-butadiene isomer repeat units in the terpolymers varied considerably with the diene concentration in the medium (Figure 3). At low diene concentration the 1,3-butadiene repeat units were almost only trans-1,4, while at higher diene concentration the amount of cis-1,4 units increased. The same behaviour was observed for ethylene-1,3-butadiene copolymerization with the same catalyst system[10].

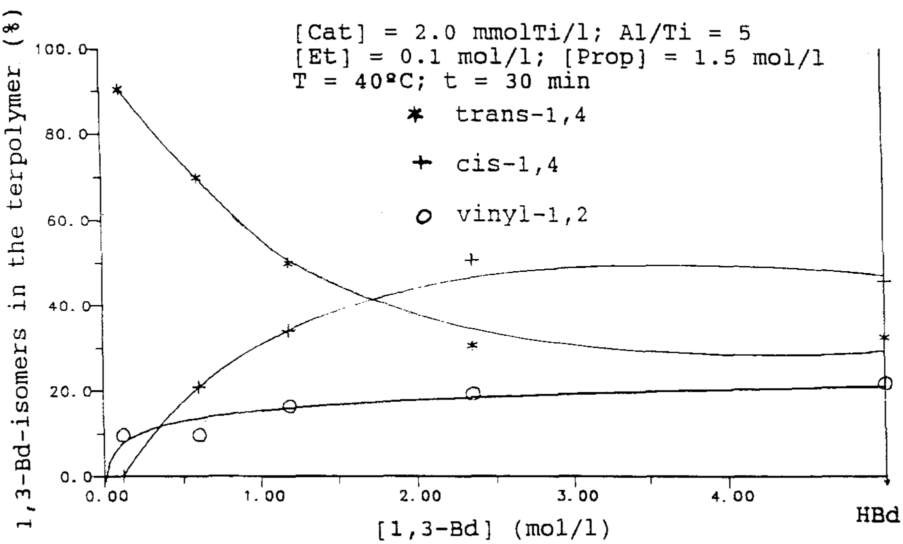

Figure 3
Influence of diene concentration on the distribution of 1,3-butadiene-isomer repeat units

Ethylene-propylene-1,5-hexadiene terpolymers

The use of 1,5-hexadiene as termonomer (diene concentration between 1.05 and 4.54 mol/l) showed that its inhibition effect on the catalyst was much smaller than with 1,3-butadiene (Figure 4). The results obtained for the terpolymerizations with 1,5-hexadiene are shown in Table 2.

The influence of diene concentration in the medium on the terpolymer composition can be seen in Figure 5. As in the previous terpolymerization, it seems that the ethylene content did not change and the propylene content decreased in the terpolymer as the 1,5-hexadiene amount increased.

The structure of the 1,5-hexadiene repeat units in the terpolymer can be discussed based on the infrared results[8,11] using the absorbance ratio A_{1650}/A_{910}. If the value of this ratio is higher than 0.30 (value of A_{1650}/A_{910} for 1,5-hexadiene homopolymer), the reaction with only one monomer double bond is favored, resulting in pendant vinylic groups in the terpolymer, in absence of cyclization

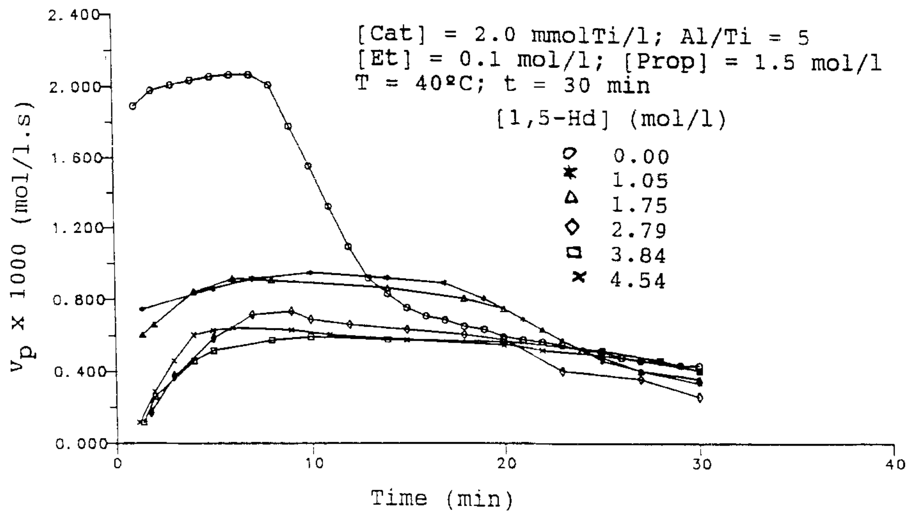

Figure 4
Influence of diene concentration on the rate of ethylene-propylene-1,5-hexadiene terpolymerization[8]

Reation #	[1,5-Hd] (mol/l)	Catalyst Activity (pPol/gTi.h)	Et (%mol)	Prop (%mol)	1,5-Hd (%mol)	A_{1650} / A_{910}
EP-03	0	1954	67.9	32.1	0	-
EPH-01	1.05	1309	72.2	19.6	8.2	0.37
EPH-02	1.75	1378	72.7	15.1	12.2	0.37
EPH-03	2.79	1330	63.7	10.1	26.1	0.33
EPH-04	3.84	1301	64.5	7.2	28.3	0.38
EPH-05	4.54	1355	64.6	5.9	29.5	0.28

Table 2
Results of ethylene-propylene-1,5-hexadiene terpolymerizations[8]

of 1,5-hexadiene (Figure 6). The absorbance ratios for the obtained terpolymers (Table 2) showed that for lower diene contents, and therefore higher propylene content, the structure 2 (Figure 6) is favored. A similar result was obtained for propylene-1,5-hexadiene copolymer[8] where in the presence of high amount of propylene incorporation the structure 2 was also the dominant one.

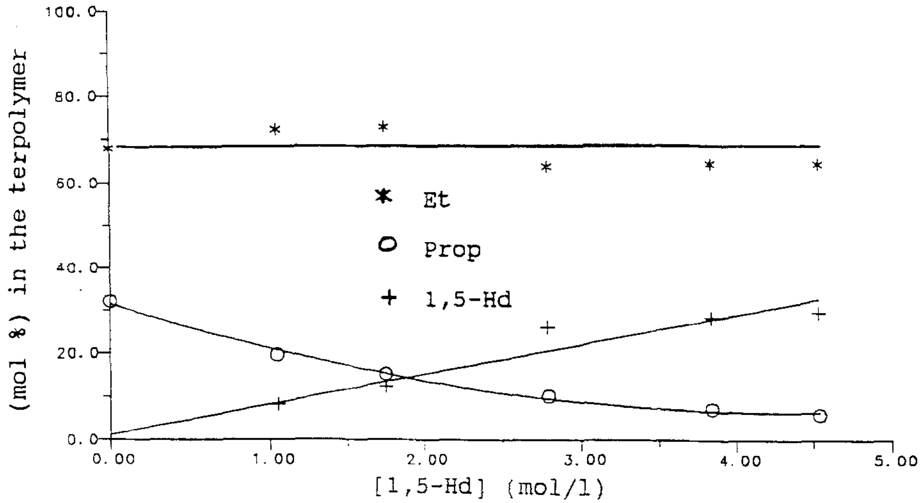

Figure 5
Influence of 1,5-hexadiene concentration on polymer composition

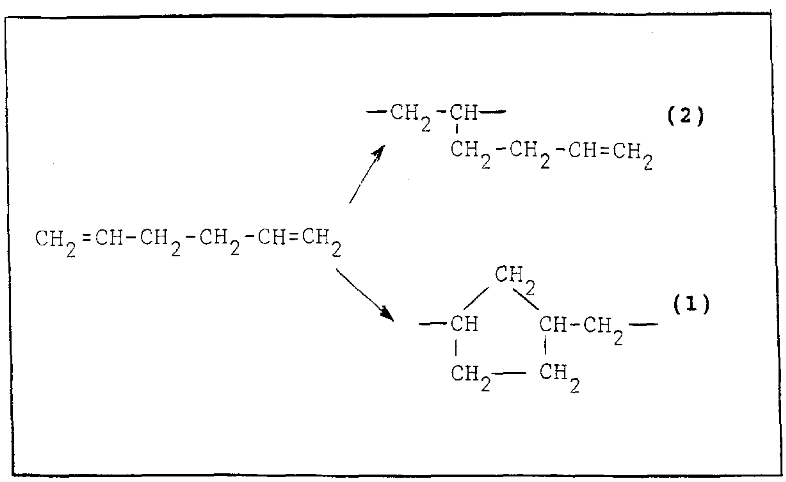

Figure 6
Structures of 1,5-hexadiene repeat units in polymers

Ethylene-propylene-1,7-octadiene terpolymers

The terpolymerizations of ethylene, propylene and 1,7-octadiene were carried out over a range of diene concentration between 0.56 and 2.78 mol/l. Figure 7 shows the influence of diene concentration in the medium on the polymerization rate. The results are summarized in Table 3.

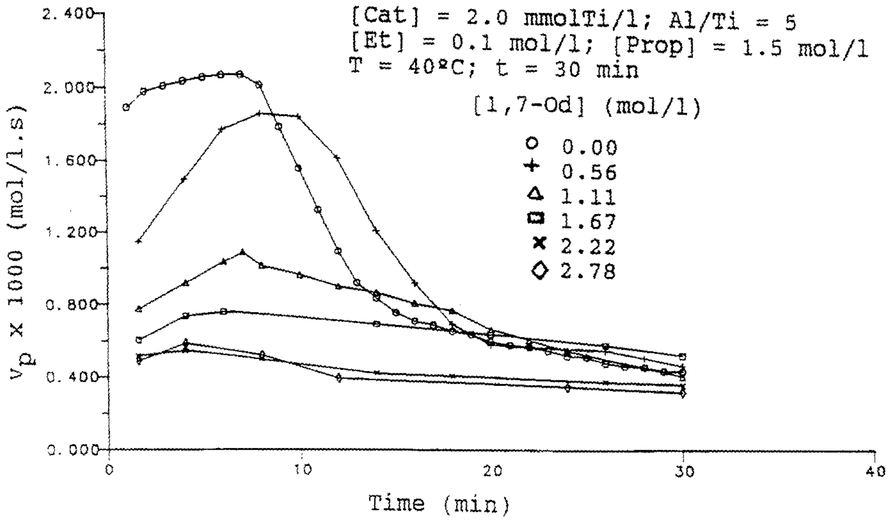

Figure 7
Influence of diene concentration on the rate of ethylene-propylene-1,7-octadiene terpolymerization[8]

Reation #	[1,7-Od] (mol/l)	Catalyst Activity (pPol/gTi.h)	Et (%mol)	Prop (%mol)	1,7-Od (%mol)
EP-03	0	1954	66.8	33.2	0
EPO-01	0.56	1728	78.2	17.0	4.8
EPO-02	1.11	1242	68.9	26.6	4.3
EPO-03	1.67	1091	78.8	14.4	6.8
EPO-04	2.22	723	79.0	13.0	8.0
EPO-05	2.78	707	80.5	11.3	8.2

Table 3
Results of ethylene-propylene-1,7-octadiene terpolymerizations[8]

The relationship between polymer composition and concentration of added diene is shown in Figure 8. Once more one can notice that the influence of the adition of higher amounts of diene in the medium on ethylene insertion in the polymer was not significant but as the diene content in the polymer increased the propylene content incorporated in the polymer chain decreased. 1,7-Octadiene repeat units in the terpolymer were found to be formed by reaction of one double bond of the monomer, introducing pendant vinyl groups in the polymer chain[8].

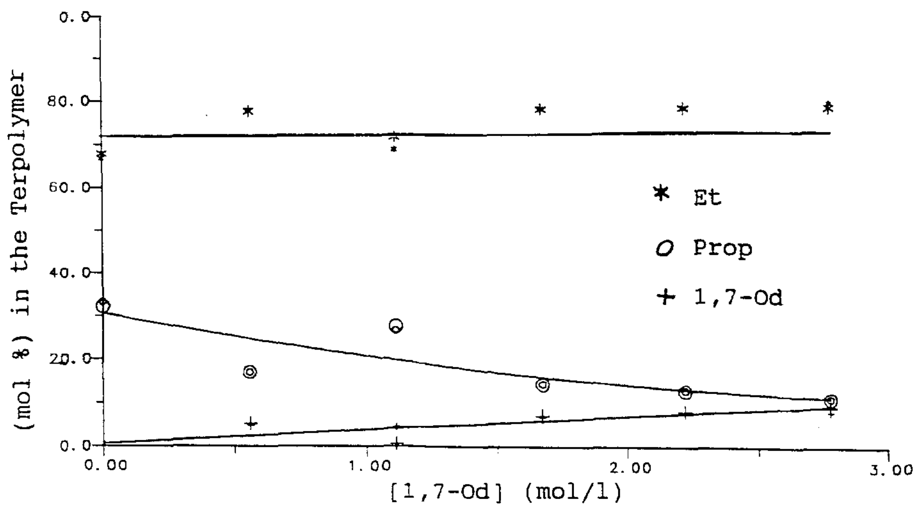

Figure 8
Influence of 1,7-octadiene concentration
on polymer composition

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