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COPOLYMERIZATION OF ETHYLENE AND BUTADIENE WITH A ZIEGLER CATALYST BASED ON $MgH_2/TiCl_4$

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Abstract—The copolymerization of ethylene and butadiene by a $MgH_2/TiCl_4$-$AlEt_3$ catalyst system was studied. The influence of diene concentration in the reaction medium and time of polymerization were described. The distribution of repeating units in the copolymers was random. The diene units were substantially in trans-1,4 configuration at lower diene content and longer polymerization times. The butadiene showed no tendency for homopolymerization with the catalyst system which was studied.

INTRODUCTION

The copolymerization of an α-olefin and a conjugated diene by means of a supported Ziegler–Natta catalyst have been recently reported [1, 2]. In spite of its practical and theoretical importance, only a few papers on this subject have been published [3–5]. The behaviour of these catalyst systems in the copolymerization with conjugated dienes is not yet fully understood. The distribution of repeating units in the copolymer is influenced by the catalyst system and polymerization conditions.

In a preceding paper [6] the copolymerizations of either ethylene or propylene with dienes were described. In that paper the effect of diene concentration on the catalyst activity was studied. The composition of the copolymers and the reactivity ratios were evaluated.

We have now carried out a study on ethylene and 1,3-butadiene copolymerization using the heterogeneous Ziegler–Natta catalyst, $MgH_2/TiCl_4$-$AlEt_3$; the microstructure of the butadiene repeating units in the copolymer was determined.

EXPERIMENTAL

Materials

Toluene was stirred over Na/K-alloy and distilled under argon. Triethylaluminium (TEA) and $TiCl_4$ were commercially obtained and used after distillation. Argon was used after passing through a molecular sieve 3 Å column. Butadiene (Bd) was passed through a molecular sieve 3 Å column and condensed before use. Ethylene (ET) was used after passing through a molecular sieve 3 Å column.

Preparation of MgH_2-supported Ti catalyst (cat): the catalyst was prepared by the procedure described elsewhere [7].

Copolymerization procedure

The copolymerizations of ethylene with butadiene were carried out in a 250 ml glass reactor (Buechi, Uster) with toluene as solvent. The catalyst suspension and the comonomer were put in the reactor at −6° and the temperature was then raised to 40°. Ethylene was introduced under a positive pressure of 530 Torr. The polymerization was initiated by injecting TEA into the reaction mixture. The rate of ethylene polymerization was followed by means of a flowmeter. The reaction was stopped by the addition of methanol.

Analytical procedures

IR spectra from polymer films were obtained with a Nicolet Instrument Fourier transform spectrometer. The distribution of isomer repeating units in polibutadiene was estimated by the method described in the literature [8]. Similarly, the composition (% w/w) and microstructure of the ethylene–butadiene copolymers were calculated as described [9]:

$$(\%\ \text{trans-1,4-Bd}) = (A_{970}/86)/x$$
$$(\%\ \text{cis-1,4-Bd}) = (A_{995}/42)/x$$
$$(\%\ \text{vinyl-1,2}) = (A_{910}/120)/x$$
$$(\%\ \text{Et}) = (A_{720}/8{,}2)/x$$
$$x = (A_{970}/86) + (A_{995}/42) + (A_{910}/120) + (A_{720}/8{,}2).$$

RESULTS

The results [10] of ethylene–butadiene copolymerizations with the catalyst system $MgH_2/TiCl_4$-$AlEt_3$ at different diene concentrations are summarized in Table 1.

It was observed that the addition of even a low amount of butadiene into the polymerization system showed a substantial effect in lowering the catalyst activity. This reduction was attributed to the stronger coordination of butadiene monomer with titanium active centres. The Ti–butenyl complex formed by that coordination is much more stable than the Ti–C σ bonds resultant from the reaction with ethylene.

Figure 1 shows the influence of diene concentration in the reaction medium on the distribution of isomers

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Table 1. Results [10] of ethylene–butadiene copolymerizations by the catalyst system $MgH_2/TiCl_4$-$AlEt_3$

Polymerization number	[Diene] in medium (molar/l)	Diene (%) in polymer (molar)	Yield (g)	Catalyst activity (gPol/gTi · hr)	Crystallinity (%)	T_m(°C)
HE-05	0	0	19.1	2215	67.4	135.7
CEB-01	0.12	1.7	1.7	197	56.9	127.7
CEB-02	0.60	8.6	0.7	81	38.3	119.4
CEB-03	1.19	12.1	1.2	138	27.2	112.8
CEB-04	2.38	19.3	1.0	112	20.4	111.4
CEB-05	3.57	20.2	1.3	146	0	—
HBd	2.38	100	0.64	73.5	—	—

[Ti] = 1.5 mmol/l; Al/Ti = 5; [Et] = 0.1 mol/l; $T = 40°$; $t = 1$ hr.

of butadiene repeating units in the ethylene copolymers.

It can be seen that the distribution of isomer repeating units in the copolymer tends to be the same as the one in the homopolymer of butadiene as the diene concentration increases. On the other hand, at low diene concentration mostly trans-1,4 isomer repeating units were found in the copoly(ethylene-butadiene). This behaviour was attributed to the isomerization of anti to sin forms in the Ti–butenyl group [11] (Fig. 2). Therefore, if the concentration of butadiene is low, the rate of diene insertion in the polymer is also low and the trans-1,4 units can also be introduced, as shown in Fig. 2, via $b' \rightarrow a' \rightarrow a''$. Consequently the content of cis-1,4 units, which would be inserted via $b' \rightarrow b''$, diminishes.

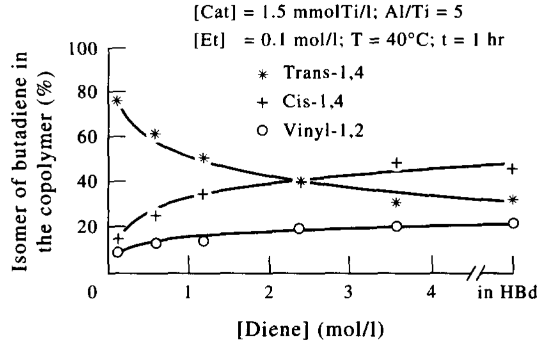

Fig. 1. Microstructure of the butadiene repeating units in the copolymers with ethylene.

The reactivity ratios for ethylene (r_1) and butadiene (r_2) were determined according to the methods of Fineman–Ross [12] and Böhm [13]. The values obtained by both methods were the same [6], i.e. $r_1 = 67$ and $r_2 = 0$, and this means that butadiene has no tendency to homopolymerization [10]. The distribution of repeating units in the copolymers was random.

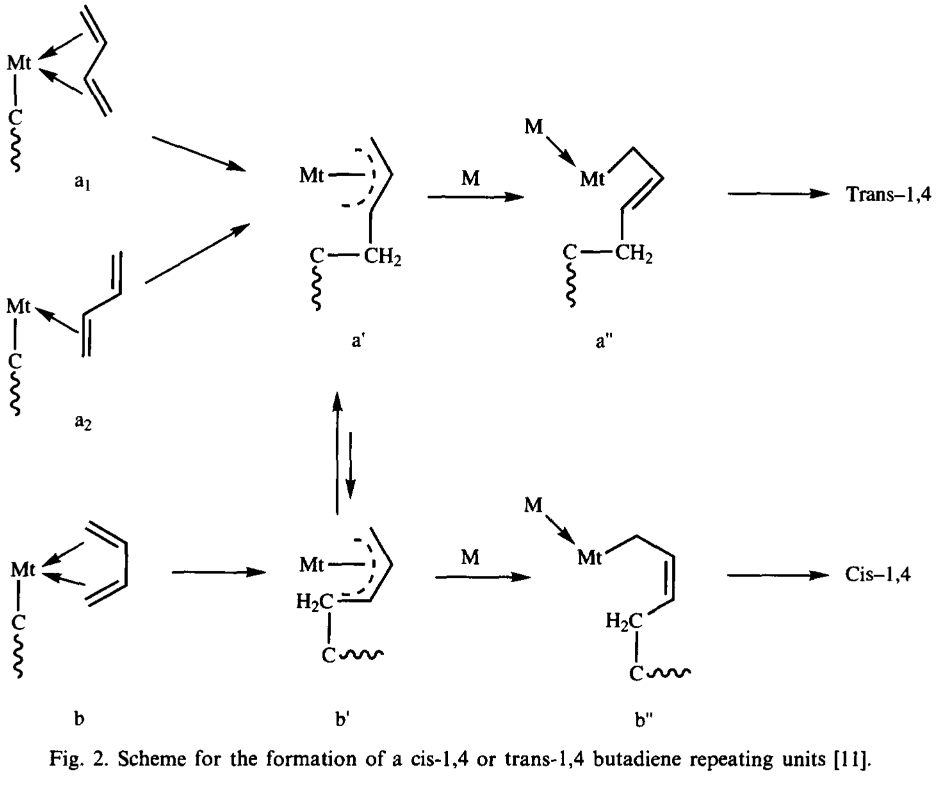

Fig. 2. Scheme for the formation of a cis-1,4 or trans-1,4 butadiene repeating units [11].

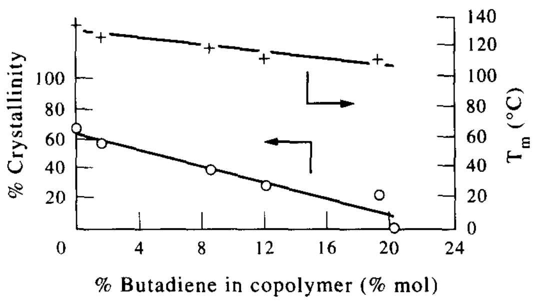

Fig. 3. Influence of butadiene content on the crystallinity and melting temperature of the copolymers with ethylene.

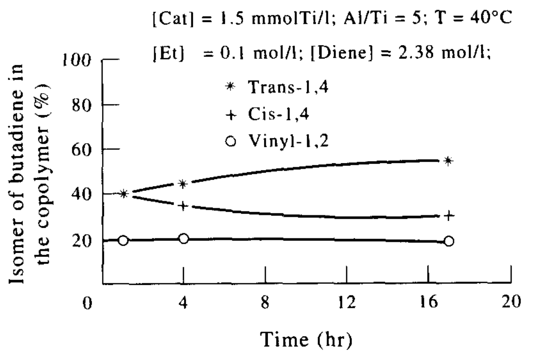

Fig. 4. Effect of reaction time on the microstructure of the butadiene repeating units in the copolymers with ethylene.

The calorimetry analysis (DSC) showed that the higher the butadiene content in the copolymer the lower is its decomposition temperature. For that reason it was impossible to carry out viscosity measurements or other analysis that requires the solubilization of the copolymers.

Figure 3 shows the influence of butadiene content on the crystallinity and melting temperature of the ethylene–butadiene copolymers [10]. Similar behaviour was found by Bruzzone *et al.* [5].

The influence of polymerization time on the catalyst activity and comonomer content [10] is presented in Table 2.

These results showed that the composition of the ethylene–butadiene copolymers remains constant between 1 and 17 hr of reaction. The content of trans-1,4-butadiene units, however, tends to increase at longer polymerization times, while the cis-1,4 units tends to decrease (Fig. 4). This behaviour strengthens the hypothesis anti to sin isomerization. Since the insertion step is slow, the anti butenyl group has time to isomerize to the more stable sin structure before monomer incorporation occurs.

Table 2. Influence of reaction time on ethylene–butadiene co-polymerization [10]

Polymerization number	Reaction time (hr)	Yield (g)	Catalyst activity (gPol/gTi · hr)	Butadiene in polymer (%molar)
CEB-04	1	1.0	112	19.3
CEB-06	4	2.4	70	19.5
CEB-07	10	2.9	33	—
CEB-08	17	4.9	33	19.1

CONCLUSION

In the copolymerizations of ethylene and butadiene with $MgH_2/TiCl_4$-$AlEt_3$ catalyst system it was observed that the addition of the diene had a strong effect in lowering the catalyst activity. It was also observed that at longer polymerization times and low diene concentrations in the reaction medium the trans-1,4 enchainment was favoured.

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