

Propene-co-butene random copolymers synthesized with superactive Ziegler–Natta catalyst

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Abstract

Temperature rising elution fractionation (TREF) was carried out on propene-co-butene random copolymers synthesized with heterogeneous Ti-based Ziegler–Natta catalysts. ¹³C-NMR and DSC measurements were carried out on the fractions. It was found that fractionation occurred on the basis of copolymer crystallizability, which is controlled by both stereoregularity and composition. This work also pointed out that such copolymers are blends of nearly Bernoullian macromolecules having different composition. Finally, a relationship between stereospecificity and comonomer reactivity appeared from the experimental data.

Keywords: Random copolymers; Temperature rising elution fractionation; Ziegler–Natta catalyst

1. Introduction

The heterogeneity in both composition and tacticity of propene copolymers from heterogeneous Ziegler–Natta catalysts is a well established feature [1–3] which has been mostly related to a broad distribution of sites having different stereospecificity and comonomer reactivity [2]. However, the relationship between stereospecificity and copolymerization reactivity is not yet completely understood, though the prevailing opinion is that the more stereospecific the site the lower its reactivity toward the comonomer [3,4].

In order to gain further insight into this problem we report and discuss in this paper some results concerning the fractionation (using the TREF technique) and the characterization (through

DSC and ¹³C-NMR measurements) of two propene-co-butene copolymers obtained from two MgCl₂/TiCl₄/DIBP catalysts widely differing in stereospecificity due to the different external donor used, namely *t*-butyl-methyl-dimethoxysilane (TBMMS) and dimethyl-dimethoxysilane (DMMS).

2. Experimental

The synthesis of the catalyst was performed according to the Ref. [6]. The homo- and copolymerizations were run in a 4 l stainless steel batch reactor. After the catalytic system was injected into the reactor, the liquid monomers were fed at 30°C. The temperature was then raised to 70°C and the polymerization was run for two hours. Hydrogen was used as molecular weight regula-

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Table 1
Synthesis of polypropene with Mg-Ti(DIBP)/TEA/silane catalyst

Donor	Yield (kg/g)	IV (dl/g)
DMMS	23	2.1
TBMMS	58	2.3

Table 2
Polypropene synthesized with Mg-Ti(DIBP)/TEA/silane catalyst. TREF on homopolymer samples

Donor	wt.%; 25°C	% mm triads	wt.%; 98°C	% mm triads	wt.%; 126°C	% mm triads
DMMS	17.6 ^a	47.4	53.7	88.5	28.7	96.6
TBMMS	1.6	37.1	6.1	82.1	92.3	99.1

Polymerization conditions: liquid monomer; 70°C; 2 h. TEA = 2.5 mmol/l; TEA/donor = 20 mole ratio; H₂ (DMMS) = 0.1 mol% (liquid phase); H₂ (TBMMS) = 0.55 mol% (liquid phase).

^a Fraction recovered through xylene solubility.

Table 3
Propylene-co-butene copolymers synthesized with Mg-Ti(DIBP)/TEA/silane catalyst

Donor	Yield (kg/g)	IV (dl/g)	XSRT ^a (wt.%)	T _m (°C)	mol% C ₄ (IR)
DMMS	7.2	2.3	40.8	132.9	8.3
TBMMS	35.4	1.7	5.6	141	9.3

Polymerization conditions: liquid monomers; 70°C; 2 h; TEA = 3 mmol/l; TEA/donor = 7.5 mole ratio; H₂ (TBMMS) = 5 mol% (gas phase); H₂ (DMMS) = 0.5 mol% (gas phase).

^a XSRT = xylene soluble at room temperature (25°C).

Table 4
Copolymers fractionation

Donor	Elution temp. (°C)	wt.%; mol% C ₄ (NMR)	mm (NMR)	C ₃ sequence length (N _p)	T _m (°C)	
TBMMS	25 ^a	5.6	17.5	0.81	5.9	97.7
	70	38	12.1	0.97	8.3	126.3
	85	37.9	7.4	0.98	13.6	140.3
	100	18.5	5	0.99	20.4	151
DMMS	25 ^a	40.8	10.8	0.6	9.8	95.2
	70	28.6	8.7	0.9	11.6	120.5
	85	20.4	5.5	0.96	18.3	137.2
	100	10	3.3	0.98	29.8	149.5
	126	0	—	—	—	—

^a Fractions recovered through xylene solubility.

tor. During the copolymerizations the monomers' concentration was kept constant through proper feeding of them. The fractionation of the polymers was made according to the TREF method that it is already described in the literature [7]. The ¹³C-NMR measurements were made according to the methods previously described [8].

3. Results

Tables 1 and 2 show the performance of the two catalysts in homopolymerization and the fractionation data relative to the homopolypropenes synthesized. The polymer from TBMMS consists mainly of highly isotactic chains together with minor amounts of low isotactic and atactic ones. In contrast, the polymer from DMMS mainly contains low isotactic chains together with a significant amount of both highly isotactic and atactic ones.

The copolymerization results are reported in Tables 3, 4 and they show that the copolymer from DMMS contains a large fraction (around 40 wt.%) soluble at 25°C and decreasing amounts of fractions eluted at higher temperatures, whereas the copolymer from TBMMS mainly consists of the fractions eluted from 70 to 100°C. The fractions differ in both composition and tacticity (mm propene triads): the butene content decreases and the mm triads increases as the elution temperature increases.

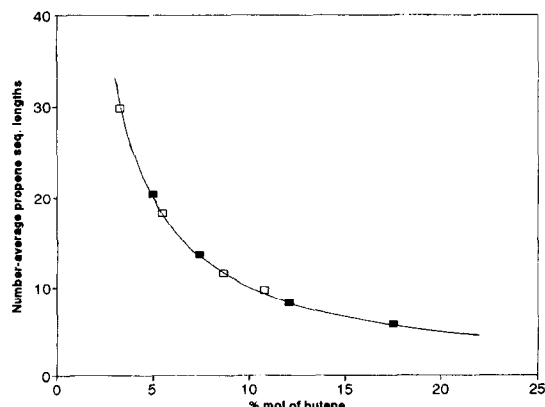


Fig. 1. The fit with the Bernoullian statistical model. — Bernoullian; ■ TBMMS; □ DMMS.

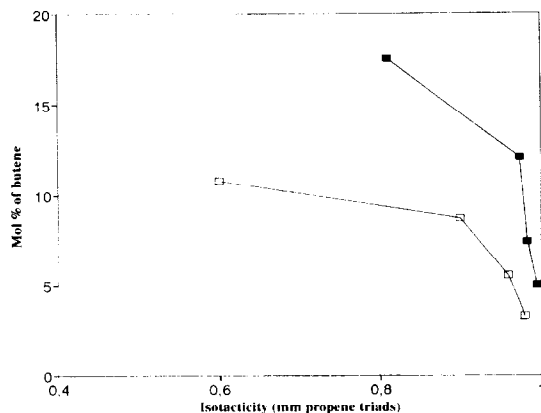


Fig. 2. The comonomer content according to the copolymer stereoregularity. ■ TBMMS; □ DMMS.

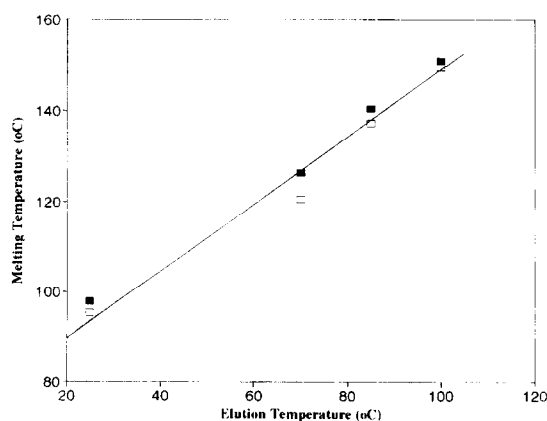


Fig. 3. TREF of propene copolymers. T_m (°C) = $75 + 0.74T_e$ (°C); $R = 0.98$. ■ TBMMS; □ DMMS.

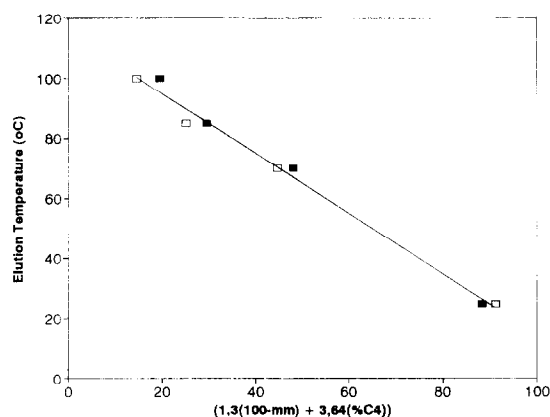


Fig. 4. TREF on random copolymers. T_e (°C) = $115 - (1.3(100 - mm) + 3.64(\%C_4))$. ■ TBMMS; □ DMMS.

Fig. 1 shows that the measured average propene sequence lengths fit well with the values predicted from the Bernoullian statistics for all the fractions

recovered, thus suggesting that the copolymers are heterogeneous mixtures of nearly random fractions. The correlation between comonomer content and stereoregularity is shown in Fig. 2: the mol% of butene decreases as the mm increases for both samples, the trend being dependent on the silane used.

4. Discussion

4.1. Fractionation mechanism

The results suggest that the fractionation of a stereoregular copolymer proceeds according to its crystallizability, as demonstrated through the linear relationship between the melting point of the fractions and the elution temperature:

$$T_m = 75 + 0.74T_e \quad (1)$$

depicted in Fig. 3. However, crystallizability and thus, fractionation, is affected by both copolymer stereoregularity and composition. As a matter of fact, it can be shown (Fig. 4) that, at least for the copolymers achieved with the present catalytic system, the elution temperature (T_e) linearly decreases as the weighed sum of the sterical errors ($100 - mm\%$), and of the butene content ($C_4\%$) (i.e. the fraction of chemical errors) increases according to an empirical equation of the type:

$$T_e = T_e^0 - (A(100 - mm\%) + B(C_4\%)) \quad (2)$$

where T_e^0 might be seen as the elution temperature of 100% isotactic polypropene and A , B give the relative contributions of the non-isotactic triads and of the comonomer units, respectively. The value found for T_e^0 , 115°C, appears quite reasonable if one takes into consideration that it was obtained by an extrapolation of experimental data, all affected by experimental errors, so that it cannot be a very precise value. On the other hand, in the literature [4] it is reported that a homopolymer having 98% of mmmm pentads elutes at 119.5°C. Further, such an equation seems to suggest that, at least for the copolymers achieved with the present catalyst, each fraction can still be a mixture of

macromolecules having different mm and $C_4\%$ values, but the same value for the combined term $A(100 - \text{mm}\%) + B(C_4\%)$; hence, it can elute at the same temperature and it can show the same melting point.

4.2. Stereospecificity/reactivity relationship

At first sight, Fig. 2 would suggest that, as already reported [1–3], there is a relationship between stereospecificity and reactivity, under the assumption that the copolymer heterogeneity faithfully reflects the sites heterogeneity. This conclusion, however, is correct only if the fractions are truly homogeneous in composition and tacticity. In this case indeed, each fraction can only arise from a family of sites having a well defined pair of values for stereospecificity and reactivity, and the conclusion that the reactivity of the sites decreases as their stereospecificity increases is consequently correct (as the curves in Fig. 2 do not coincide, it must be concluded that sites from different catalysts may not be equivalent). On the other hand, the trend of Fig. 2 can on principle be observed even though the fractions are not homogeneous, owing to the fact that, based on the fractionation technique, fractions having a progressively lower *average* comonomer content and higher *average* isotacticity are likely to be separated as the elution temperature increases. If so, however, no close relationship between reactivity and stereospecificity can be established, because (as it can be argued from Eq. 2) sites with the same stereospecificity can produce chains having a broad spectrum of composition. At this time it is not easy to ascertain whether the fractions are truly homogeneous in composition or not. However, some evidence in favour of the compositional homogeneity of the fractions can be deduced from the fact that the sequences distribution of all the fractions conform rather well to the Bernoullian statistics (see Fig. 1). As a matter of fact, it has already been shown that compositionally heterogeneous polymers usually deviate from the completely random model even though the individual chains are truly Bernoullian [5].

The conclusion that the comonomer reactivity is closely related to the site stereospecificity appears thus slightly favoured by the present results. However, it is worth noting, in Fig. 2, that sites showing small differences in stereospecificity (96–99 of mm triads) can show widely different reactivity. The same behaviour is exhibited by sites having the same stereospecificity, but belonging to different catalysts. This probably reflects a different acidity and/or a different stereochemical environment of the sites.

5. Conclusions

From this discussion it can be concluded that:

- (i) the TREF technique does not necessarily afford fractions with a narrow distribution of composition and stereoregularity, at least when it is applied to propene-co-butene random copolymers.
- (ii) a relationship between the copolymerization reactivity of the sites and their stereospecificity would appear from the experimental data; on the other hand, it could be stated only if the fractions are truly homogeneous.
- (iii) some support to the fractions homogeneity can be found in the result of the test for the conformity to the Bernoullian statistics. As a consequence, the suggested reactivity/stereospecificity correlation appears likely to hold true, at least as far as an individual catalytic system is considered.
- (iv) finally, one could say that these propene-co-butene random copolymers are blends of nearly random copolymers with different compositions.

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References

- [1] S. van der Ven, *Polypropylene and Other Polyolefins*, Elsevier, Amsterdam, 1990, Chaps. 3, 4 and references therein.
- [2] H.N. Cheng and M. Kakugo, *Macromolecules*, 24 (1991) 1724; P. Locatelli, M.C. Sacchi, I. Tritto and G. Zannoni, *Makromol. Chem., Rapid Commun.*, 9 (1988) 575.
- [3] M. Kakugo, T. Miyatake and K. Mizunuma, *Macromolecules*, 24 (1991) 1469.
- [4] M. Kakugo, T. Miyatake, K. Mizunuma and Y. Kawai, *Macromolecules*, 21 (1988) 314.
- [5] C. Cozewith, *Macromolecules*, 20 (1987) 1237.
- [6] *Ore. Pat.* 45977.
- [7] L. Wild, *Adv. Polym. Sci.*, 98 (1990) 1.
- [8] J.C. Randall, *Macromolecules*, 11 (1978) 592; H.N. Cheng, *J. Polym. Sci.*, 4 (1983) 573.