Ethylene Copolymerization with Long Chain α -Olefins; Binary Reactivity Ratios

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Ethylene copolymers with C_{10} , C_{12} and C_{16} α -olefins were prepared with slurry polymerization using Ziegler-Natta catalysts. The polymer composition was analyzed by ^{13}C NMR spectroscopy. The binary reactivity ratios were determined by minimizing the squares of the differences between the analyzed and calculated compositions. The reliability of the determined binary reactivity ratios was estimated using 95 % joint confidence limits. The binary reactivity ratios were compared to the reactivity ratios of the same monomer pairs determined in terpolymerizations, which have been reported elsewhere.

Introduction

The copolymerization of ethylene with linear α -olefins has found wide industrial applications in the synthesis of branched polyethylene structures in a low pressure using coordination catalysts.

For the calculation of polymer composition in such polymerizations, copolymerization equations have been applied^{1,2}. In a two-component copolymerization there are several methods for determination of the reactivity ratios,^{1,3–10}. In binary copolymerizations of ethylene with short chain α -olefins (C_4 ... C_8), the reactivity ratios have been studied extensively. The reactivity ratios of ethylene with long chain α -olefins are less well known. In this study the copolymerization of ethylene with C_{10} , C_{12} and C_{16} α -olefins has been investigated in slurry polymerization, and the reactivity ratios for pairs ethylene- α -olefin have been determined. Additionally 95 % joint confidence limits have been calculated for these reactivity ratios.

Experimental

The slurry polymerizations were carried out in a *n*-heptane reaction medium at 90°C in a 1 dm³ stirred autoclave. The semibatch ethylene addition kept ethylene partial pressure in the reactor

constant. The comonomer was added batchwise before the ethylene addition. The conversions of comonomers were always less than 10 %, the drift in comonomer concentration causing an insignificant effect to the steady conditions in the reactor. The Ziegler-Natta catalyst was a commercial $\text{TiCl}_3 \cdot 1/3 \text{ AlCl}_3$ catalyst and the cocatalyst was Et_3Al . The molar Al/Ti ratio was 10. The polymerization procedure and the analytical methods employed have been described earlier¹¹.

The comonomer contents in polymers were determined by ^{13}C NMR spectroscopy. The concentrations of branches caused by the long chain α -olefins could be determined by this method because only one comonomer was used in each polymerization. Spectra were run on a JEOL FX 90 Q pulse Fourier transform spectrometer. Samples were 20 wt-% solutions in trichlorobenzene at 160°C. Broad band noise decoupling was employed. Instrumental conditions: pulse width 45°, pulse repetition 3s, spectral width 3000 Hz, number of scans 3000–10000. The peaks in the spectra of ethylene copolymers with long chain α -olefins were identified from the chemical shifts at 38.3, 34.6, 32.2, 30.4, 27.3, 22.8 and 14.1 ppm¹². Detailed information was published in reference 11. The reproducibility of the determinations was ± 0.5 wt-%.

Fig. 1 shows monomer molar ratios in copo-

Fig. 1. Dependence of monomer molar ratios in the copolymer samples on molar ratios initially in the reactor.

c_1 = ethylene concentration in reactor, c_2 = comonomer concentration in reactor, n_2/n_1 = molar ratio of comonomer to ethylene in copolymer.

Comonomers: $\square$ = 1-decene
 $+$ = 1-dodecene
 $\circ$ = 1-hexadecene

lymers as a function of molar ratios in the reactor. We can see that the dependence is linear, and that the slope depends on the comonomer employed.

The reactivity ratios r_1 and r_2 were determined for each ethylene – comonomer pair from the experimental data. The determination was carried out by a computer with a nonlinear optimization algorithm by adjusting the reactivity ratios so that the squares of the sums of the differences between the experimentally analyzed and calculated comonomer contents were minimized.

The nonlinear SIMPLEX algorithm used was originally developed by Nelder and Mead¹³. The version used here was published by Fredenslund *et al.*¹⁴.

Table 1. Determined binary reactivity ratios in copolymerization of ethylene with C_{10} , C_{12} and C_{16} α -olefins.

Monomer pair	r_1	r_2
Ethylene–1-decene	240	0.010
Ethylene–1-dodecene	350	0.018
Ethylene–1-hexadecene	490	0.019

The comonomer mole fractions in copolymers were calculated with the following Equation¹⁵:

Table 2. Comparison of experimental and calculated polymer compositions.

Polymerization conditions: catalyst $TiCl_3 \cdot 1/3 AlCl_3$, cocatalyst Et_3Al , polymerization temperature 90 °C, reaction time 2 h, hydrogen partial pressure 300 kPa.

Experimental mole fractions In the reactor		Calculated mole fractions in polymers	
Ethylene	α -Olefin	α -Olefin	α -Olefin
	1-Decene	1-Decene	1-Decene
0.51	0.49	0.0041	0.0041
0.51	0.49	0.0047	0.0041
0.50	0.50	0.0049	0.0042
0.50	0.50	0.0043	0.0042
0.23	0.77	0.0115	0.0139
0.33	0.67	0.0098	0.0084
0.25	0.75	0.0137	0.0126
0.14	0.86	0.0253	0.0252
0.08	0.92	0.0476	0.0506
Sum of the squares of the differences = $3.2 \cdot 10^{-5}$			
	1-Dodecene	1-Dodecene	1-Dodecene
0.38	0.63	0.0034	0.0049
0.50	0.50	0.0031	0.0029
0.53	0.47	0.0020	0.0025
0.33	0.67	0.0082	0.0059
0.29	0.71	0.0064	0.0074
0.23	0.77	0.0098	0.0099
0.25	0.75	0.0074	0.0089
0.14	0.86	0.0194	0.0185
0.08	0.92	0.0381	0.0394
Sum of the squares of the differences = $2.0 \cdot 10^{-5}$			
	1-Hexa- decene	1-Hexa- decene	1-Hexa- decene
0.29	0.71	0.0052	0.0051
0.36	0.64	0.0045	0.0038
0.50	0.50	0.0014	0.0021
0.59	0.41	0.0006	0.0014
0.27	0.73	0.0056	0.0057
0.14	0.86	0.0128	0.0133
0.25	0.75	0.0065	0.0064
0.08	0.92	0.0208	0.0205
Sum of the squares of the differences = $2.0 \cdot 10^{-6}$

Fig. 2. Calculated 95 % joint confidence limit loops. Monomer pairs: a. ethylene-1-decene, b. ethylene-1-dodecene, c. ethylene-1-hexadecene.

○ = determined binary reactivity ratios

× = determined reactivity ratios based on terpolymerization experiments in reference 17.

$$\frac{n_2}{n_2 + n_1} = \frac{(r_2 M_2^2 + M_2 M_1)}{(r_2 M_2^2 + 2M_1 M_2 + r_1 M_1^2)} \quad (1)$$

where n_1 , n_2 = moles per unit weight of ethylene and comonomer respectively in a polymer sample.

M_1 , M_2 = initial mole fraction of ethylene and comonomer respectively in the reactor.

The determined reactivity ratios appear in Table 1. Using these reactivity ratios and Equation 1 the comonomer molar fractions in copolymer samples were calculated. The calculated molar fractions have been compared to the experimentally analyzed molar fractions in Table 2, where the reaction conditions are also indicated.

Because the number of experiments is limited and the experimental work has some uncertainties, the reactivity ratios should be cited as numbers with associated confidence limits. The experimental uncertainty of r_1 and r_2 is directly related. Thus, the preferred method to indicate reliability is to calculate 95% joint confidence limits^{7,16}.

Joint confidence limit loops are calculated according to Equation 11 in reference 7. The calcu-

lated loops for the three sets of experiments are shown in Fig. 2a, b and c.

Discussion

In reference 17 the terpolymerization of ethylene with 1-butene and long chain α -olefins was studied. For these terpolymerizations the reactivity ratios were determined by a nonlinear computer search, without the assumption that binary reactivity ratios could be applied to the terpolymerization equation.

In comparison of the ethylene – long chain α -olefin reactivity ratios determined with the terpolymerization data to the binary reactivity ratios, we can notice that the values of reactivity ratios are within the corresponding joint confidence limit loops of binary reactivity ratios. The reactivity ratios determined earlier with terpolymerizations are indicated in Figure 2a, b and c according to reference 17. The calculated joint confidence limit loops are narrow in their shape, which indicates that probable r_1 and r_2 values are coupled to each other.

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