$[CH_2C_6H_4CH{=}CH_2]Cl^-$ (homopolymer), 98065-26-0.

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Ethylene Terpolymerization with 1-Butene and Long-Chain α-Olefins: Reactivity Ratios

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ABSTRACT: The terpolymerization equation has been applied to ethylene terpolymerization with 1-butene and C_{10}, C_{12}, and C_{16} α-olefins. The six binary reactivity ratios in the terpolymerization equation were determined by a computer search for each terpolymerization. The calculated polymer compositions were compared with the compositions determined by ^{13}C NMR spectroscopy, and the results generally agreed within 1 wt %. The terpolymerization behavior could be explained with the determined reactivity ratios and the terpolymerization equation.

Introduction

The copolymerization of ethylene with linear α-olefins has recently found wide industrial applications in the synthesis of branched polyethylenes under low pressure using Ziegler–Natta catalysts.

In the calculation of Ziegler–Natta-type polymerizations, copolymerization equations have been successfully applied.[1,2] In a two-component copolymerization, several methods have been developed for the determination of the reactivity ratios.[1,3-10] In the case of terpolymerization, the situation is more complicated so computer-searching algorithms have been applied.[11-13]

In the binary copolymerizations of ethylene with different α-olefins, the reactivity ratios have been studied rather extensively.[14-22] For terpolymerizations of ethylene with 1-butene and long (C_{10}–C_{16}) α-olefins, a synergistic effect has been reported in the reactivities of 1-butene and the long-chain α-olefins,[23-25] though reactivity ratios for this case had not been determined earlier.

Experimental Section

In slurry-type coordination polymerizations, the reaction medium was *n*-heptane. $TiCl_3 \cdot {}^1/_3AlCl_3$ was used as the catalyst and Et_3Al as cocatalyst. 1-Butene, 1-decene, 1-dodecene, and 1-hexadecene were employed as comonomers with ethylene. The polymerization temperature was 90 °C and the hydrogen partial pressure 300 kPa. The steady-state conditions were approximated by keeping the comonomer conversions always less than 15% and by adding ethylene in a semibatch way. The polymerization procedures and the analytical methods have been reported elsewhere.[23-25]

It has shown previously that monomer concentrations in polymerizations have a synergistic effect on the comonomers and, thus, the composition of the polymer product. The reactivity of the long α-olefins in the presence of 1-butene has been considerably higher than could be assumed based on binary ethylene–α-olefin copolymerizations.[23-25] The effect of 1-butene addition on ethylene copolymerization with 1-dodecene can be seen clearly in Figure 1.

It is often assumed that terpolymerization can be calculated with the simple terpolymerization equation using reactivity ratios determined with binary copolymerizations.[26-30] That assumption is unnecessary when the six reactivity ratios in the terpolymerization equation are searched by a computer algorithm. In this algorithm, the binary reactivity ratios (r_{ij}) are adjusted to give the most suitable compositions calculated with the terpolymerization equations. The sum of the squares of the deviations can be used as the function to be minimized.

The SIMPLEX algorithm was applied for estimation of parameters of nonlinear models. It was originally developed by Nelder and Mead,[31] though the version used in this study has been published by Fredenslund et al.[32]

A simple terpolymerization equation developed by Alfrey and Goldfinger[26] was used in the form

$$\mathrm{d}c_1/\mathrm{d}c_3 = \{c_1(c_1r_{23}r_{32} + c_2r_{31}r_{23} + c_3r_{32}r_{21}) \times (c_1r_{12}r_{13} + c_2r_{13} + c_3r_{12})\}/\{c_3(c_1r_{12}r_{23} + c_2r_{13}r_{21} + c_3r_{12}r_{21})(c_3r_{31}r_{32} + c_1r_{32} + c_2r_{31})\} \quad (1)$$

$$\mathrm{d}c_2/\mathrm{d}c_3 = \{c_2(c_1r_{32}r_{13} + c_2r_{13}r_{31} + c_3r_{12}r_{31}) \times (c_2r_{21}r_{23} + c_1r_{23} + c_3r_{21})\}/\{c_3(c_1r_{12}r_{23} + c_2r_{13}r_{21} + c_3r_{12}r_{21})(c_3r_{31}r_{32} + c_1r_{32} + c_2r_{31})\} \quad (2)$$

where c_i is the molar concentration of monomer i (i = 1, 2, 3) and r_{ij} ($i \neq j$) is the appropriate binary reactivity ratio. In the present case subscripts 1, 2, and 3 refer to ethylene, 1-butene, and the long-chain α-olefin, respectively. The compositions of terpolymers prepared in sta-

Table I
Reactivity Ratio Ranges

terpolymer	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
ethylene–1-butene–1-decene	40 ± 5	0.02 ± 0.02	230 ± 20	0.03 ± 0.03	0.1 ± 0.1	0.1 ± 0.1
ethylene–1-butene–1-dodecene	40 ± 5	0.02 ± 0.02	360 ± 20	0.03 ± 0.03	0.1 ± 0.1	0.3 ± 0.3
ethylene–1-butene–1-hexadecene	40 ± 5	0.02 ± 0.02	420 ± 20	0.03 ± 0.03	0.1 ± 0.1	0.5 ± 0.5

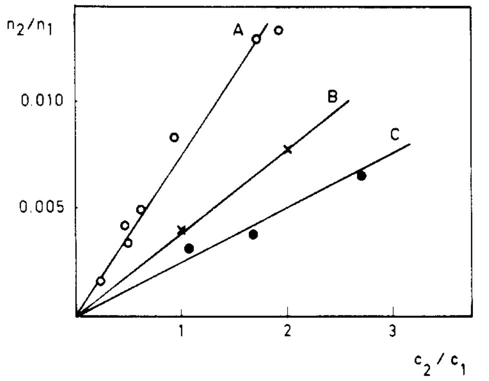

Figure 1. Effect of 1-butene addition on the ethylene copolymerization with 1-dodecene. n_2/n_1 = molar ratio in polymer and c_2/c_1 = molar ratio in the reactor, where 1 = ethylene and 2 = 1-dodecene. 1-Butene concentrations in the reactor: (A) 0.5 mol/dm^3; (B) 0.2 mol/dm^3; (C) no 1-butene.

tionary conditions can be calculated with these equations.

The minimized square sum was applied in the form

$$f = \sum_{i=1}^{n} [(m_{\mathrm{but},i} - m'_{\mathrm{but},i})^2 + (m_{\mathrm{ol},i} - m'_{\mathrm{ol},i})^2] \qquad (3)$$

where n is the number of experimental points, m is the calculated comonomer content in polymer, and m' is the experimental comonomer content in polymer.

Table I presents the reactivity ratios calculated for the following terpolymers: ethylene–1-butene–1-decene, ethylene–1-butene–1-dodecene, and ethylene–1-butene–1-hexadecene. The polymerization reaction concentrations and the comonomer contents measured by ^{13}C NMR spectroscopy from the experimental samples are given in Table II. These values have been compared with the compositions calculated with the given exact reactivity ratios.

The calculated comonomer contents usually agreed within ±1 wt % with the analyzed contents. This accuracy is of the same order as the reproducibility of the polymerizations and the analytical methods. Because of the monomer reactivities the experiments had to be limited to the range of low comonomer contents in polymers. This causes the values of r_{21}, r_{31}, and r_{32} to be less accurate than the other r values. When estimating the accuracy of the results, one has to notice that the amount of experimental material is limited and the analytical uncertainty in copolymer composition is approximately ±0.5 wt %.

Discussion of Results

Based on the calculated reactivity ratios, polymerization monomer concentrations can be correlated to the polymer compositions, and thus, the interdependencies between monomers can be explained. In Figure 2, the calculated comonomer contents of ethylene–1-butene–1-dodecene terpolymers have been graphed as the 1-butene concentration in the reactor varies. The calculation is based on the reactivity ratios presented in Table I and eq 1 and 2. The synergistic effect between 1-butene and 1-dodecene can be clearly seen.

The effect of the 1-dodecene concentration in the polymerization reactor on polymer composition is presented

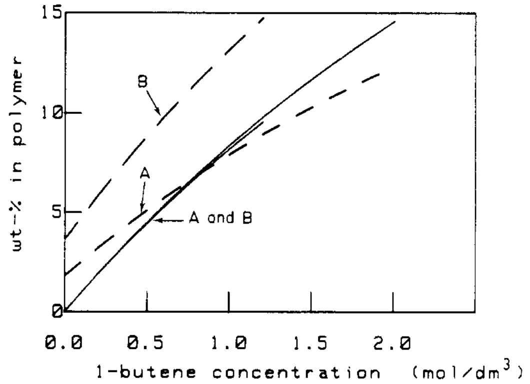

Figure 2. Effect of 1-butene concentration in the reactor on polymer comonomer contents in the ethylene copolymerization with 1-butene and 1-dodecene, calculated with eq 1 and 2: (—) 1-butene, r_{12} = 41, r_{13} = 340, r_{23} = 0.015; (– –) 1-dodecene, r_{21} = 0.005, r_{31} = 0.036, r_{32} = 0.277. Concentrations of ethylene [Et] and 1-dodecene [Dod] in mol/dm^3: (A) [Et] = 0.5, [Dod] = 0.5; (B) [Et] = 0.5, [Dod] = 1.0.

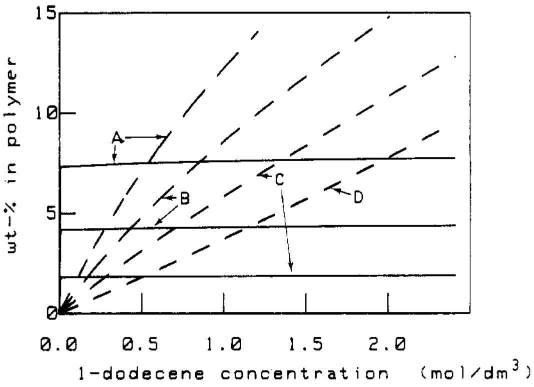

Figure 3. Effect of 1-dodecene concentration in the reactor on the polymer composition, calculated with eq 1 and 2: (—) 1-butene, r_{12} = 41, r_{13} = 340, r_{23} = 0.015; (– –) 1-dodecene, r_{21} = 0.005, r_{31} = 0.036, r_{32} = 0.277. Concentrations of ethylene [Et] and 1-butene [But] in mol/dm^3: (A) [Et] = 0.5, [But] = 1.0; (B) [Et] = 0.5, [But] = 0.5; (C) [Et] = 0.5, [But] = 0.2; (D) [Et] = 0.5, [But] = 0.

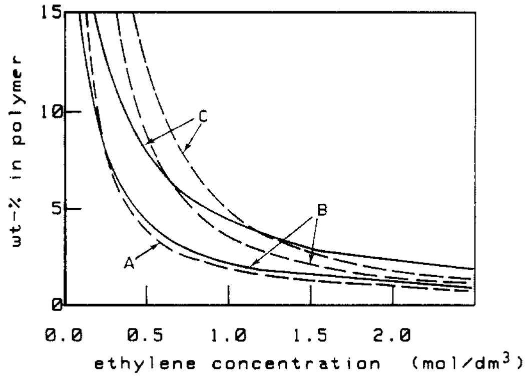

Figure 4. Effect of ethylene concentration in the reactor on polymer composition calculated with eq 1 and 2: (—) 1-butene, r_{12} = 41, r_{13} = 340, r_{23} = 0.015; (– –) 1-dodecene, r_{21} = 0.005, r_{31} = 0.036, r_{32} = 0.277. Concentrations of 1-butene [But] and 1-dodecene [Dod] in mol/dm^3: (A) [But] = 0, [Dod] = 1; (B) [But] = 0.5, [Dod] = 1; (C) [But] = 1.0, [Dod] = 1.

Table II
Comparison of Analyzed Comonomer Contents to Contents Calculated with Terpolymerization Equation[a]

A. Terpolymerization with 1-Decene[b]

concn in reactor, mol/dm^3			contents in polym, wt %			
			exptl		calcd	
[Et]	[But]	[Dec]	But	Dec	But	Dec
0.50		0.48		2.0		1.9
0.50		0.48		2.3		1.9
0.30		1.0		5.5		6.3
0.55	0.03	0.48	0.5	2.0	0.3	2.0
0.50	0.06	0.48	1	3.3	0.6	2.4
0.35	0.18	0.48	2.5	6.6	2.5	5.4
0.47	0.48	0.12	4.7	2.3	4.9	2.1
0.47	0.48	0.24	4.9	2.7	4.9	3.8
0.45	0.48	0.24	4.5	4.8	5.1	4.0
0.18	0.50	0.50	12	22	11	21
0.29	0.50	0.50	5.7	10	7.7	12
0.37	0.50	0.50	8.2	10	6.3	9.2
0.46	0.50	0.50	6.1	7.0	5.1	7.0
0.52	0.50	0.50	4.1	6.0	4.6	7.0
0.55	0.48	0.48	4.5	5.7	4.2	5.2

B. Terpolymerization with 1-Dodecene[c]

concn in reactor, mol/dm^3			contents in polym, wt %			
[Et]	[But]	[Dod]	But	Dod	But	Dod
0.25		0.50		4.7		3.6
0.55		0.48		1.2		1.6
0.64		1.5		3.7		4.3
0.50	0.03	0.48	0.9	3.5	0.3	1.9
0.60	0.03	0.50	0.7	2.5	0.2	1.6
0.14	0.06	0.48	1.6	9.6	2.0	9.4
0.50	0.06	0.50	1.3	2.6	0.6	2.2
0.55	0.10	0.50	1.1	0.7	0.9	2.2
0.22	0.18	0.48	4.6	7.4	3.7	8.5
0.56	0.18	1.0	1.6	4.1	1.5	4.9
0.23	0.30	0.48	5.0	10	5.6	11
0.57	0.48	0.12	3.4	0.7	3.9	1.1
0.53	0.50	0.20	4.1	1.9	4.3	2.1
0.55	0.48	0.24	3.0	2.3	4.0	2.3
0.48	0.48	0.24	5.4	2.8	4.5	2.8
0.17	0.50	0.50	8.6	22	11	21
0.30	0.48	0.48	7.0	8.5	6.8	9.8
0.30	0.48	0.48	6.0	10	6.8	9.8
0.35	0.48	0.48	6.2	8.0	6.0	8.0
0.38	0.48	0.73	5.3	8.0	5.5	9.8
0.25	0.50	0.50	8.4	15	8.2	13
0.55	0.50	1.0	3.9	7.2	4.1	7.8
0.42	0.66	0.48	6.7	8.1	6.8	7.5

C. Terpolymerization with 1-Hexadecene[d]

concn in reactor, mol/dm^3			contents in polym, wt %			
[Et]	[But]	[Hexad]	But	Hexad	But	Hexad
0.20		0.48		4.0		4.3
0.25		0.45		3.5		3.3
0.50		0.50		1.1		1.8
0.70		0.48		0.5		1.3
0.30		0.80		4.3		4.8
0.35	0.03	0.48	0.5	4.5	0.4	3.4
0.40	0.06	0.48	1.0	5.1	0.8	3.6
0.47	0.18	0.48	1.8	6.1	1.9	5.2
0.30	0.48	0.24	6.8	12	7.1	12
0.40	0.48	0.48	5.1	11	5.5	13
0.48	0.50	0.50	5.5	12	4.8	11
0.27	0.50	0.50	7.3	22	7.8	21
0.37	0.50	0.50	6.4	14	6.0	15
0.45	0.48	0.12	6.1	3.9	5.0	4.0

[a] Et = ethylene, But = 1-butene, Dec = 1-decene, Dod = 1-dodecene, Hexad = 1-hexadecene. [b] $r_{12} = 39$, $r_{13} = 245$, $r_{23} = 0.33$, $r_{21} = 0.02$, $r_{31} = 0.003$, $r_{32} = 0.019$; sum of squared deviations = 22.3. [c] $r_{12} = 41$, $r_{13} = 340$, $r_{23} = 0.015$, $r_{21} = 0.005$, $r_{31} = 0.036$, $r_{32} = 0.277$; sum of squared deviations = 25.6. [d] $r_{12} = 39$, $r_{13} = 432$, $r_{23} = 0.010$, $r_{21} = 0.008$, $r_{31} = 0.010$, $r_{32} = 0.056$; sum of squared deviations = 14.0.

in Figure 3. One can see that the 1-butene content in the polymer decreases slightly as the 1-dodecene concentration in the reactor increases.

The effect of ethylene concentration in the reactor on comonomer contents of the polymer can be seen in Figure 4. A change in the ethylene partial pressure, and thus in the ethylene concentration, has a substantial effect on the comonomer contents of polymers at partial pressures corresponding to concentrations below 2 mol/dm^3 of ethylene in the reactor and even more noticeably below 1 mol/dm^3.

At small ethylene concentrations the synergism of 1-butene and 1-dodecene is most apparent. The lower the ethylene partial pressure, the lower the 1-butene concentration needed to substantially increase the 1-dodecene concentration in the polymer. Synergism cannot be detected at higher ethylene concentrations, which is in accordance with the experimental results.

It can be demonstrated experimentally that the reaction rate in the binary copolymerization of 1-butene/1-dodecene is very small. It is probable that the constants r_{23} and r_{32} do not represent the direct reaction between 1-butene and long-chain α-olefin. Evidently they represent the reactions of α-olefins in the vicinity of a branch in the polymer chain, which means that there operates a penultimate effect.

One has to notice that the growth of polymer particles in a heterogeneous polymerization causes some uncertainity as to the steady-state assumption. The deviations between the calculated and analytically measured comonomer contents are partly due to experimental errors and partly due to the inaccuracy of the steady-state assumption in a heterogeneous system. Since the calculated compositions agree rather well with the analyzed compositions, the steady-state approximation seems to be reasonable.

It is often assumed that heterogeneous Ziegler–Natta catalysts contain active centers of different activities. In this paper has been assumed that the reactivity ratios however remain constant. In the case of a distribution also in the reactivity ratios the average method described in this paper is not valid.

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Registry No. Ethylene, 74-85-1; 1-butene, 106-98-9; 1-decene, 872-05-9; 1-dodecene, 112-41-4; 1-hexadecene, 629-73-2.

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Photochemical Properties of Rose Bengal. 11. Fundamental Studies in Heterogeneous Energy Transfer

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ABSTRACT: Polymers deriving from nucleophilic displacement by rose bengal on poly(styrene-*co*-vinylbenzyl chloride) are studied as heterogeneous energy-transfer donors to oxygen. Self-quenching of rose bengal excited states by proximate rose bengal ground states is observed both in the singlet and in the triplet regime. These self-quenching effects are more significant for powders than they are for the same polymers in solution and affect the quantum yield of singlet oxygen formation. The rose bengal triplet lifetime for the poly-RB's is longer (1.5 ms) than is the lifetime of rose bengal in EtOH (90 μs). Upon irradiation in thick films an even longer lifetime product, which may be either a reduced quinomethine, a triphenylmethyl radical, or a radical ion, is observed. Formation of this intermediate is accompanied by cross-linking of the poly-RB matrix.

Introduction

The first use of an insoluble polymer bead as a support for rose bengal and its use as a photosensitizer was reported by Neckers, Schaap, and co-workers in 1978.[1,2] Their idea was conceptually based on Merrifield chemistry, i.e., solid-phase synthesis.[3-5] The original polymer-supported singlet oxygen sensitizer, called Ⓟ-rose bengal, could be used to form singlet oxygen in solvents in which rose bengal itself was not soluble[1,2] since the hydrophobic polymer support carried the basically polar dye into these nonpolar media. Ⓟ-Rose bengal could also be used in polar solvents.[6]

There are several ways to prepare polymer-based sensitizers from xanthene dyes. The sensitizer may be covalently bound to the polymer support.[1,3,7] Rose bengal is a xanthene dye that behaves as a nucleophile at the C-2′ carboxylate. The sensitizer may be absorbed onto a polymeric support.[8,9] The sensitizer may be incorporated into a polymeric film.[10,11] Or the sensitizer may be immobilized with an ion-exchange resin.[12]

We concentrate in this publication on the properties of rose bengal immobilized by covalent bonding to poly(styrene-*co*-vinylbenzyl chloride)—the soluble polymer analogous to Merrifield's resin. It is our purpose to assess the effect of polymer structure and the relationship and proximity of immobilized dye molecules on the photochemistry and the spectroscopy of the polymeric reagent.

The original polymer rose bengal produced singlet oxygen in methylene chloride but with a lower quantum yield (0.43) than did the dye dissolved in methanol (0.76). Lamberts and Neckers[13-15] established that rose bengal could be converted, using standard organic reactions, to monomeric derivatives that were soluble and produced singlet oxygen, in both nonpolar and polar solvents. These derivatives showed very similar quantum yields, and the essential component of the sensitizer molecule was shown to be the fully developed xanthene chromophore. Since rose bengal derivatives are usually soluble in methanol, they could be shown to produce singlet oxygen with essentially the same quantum yield that rose bengal dye (the disodium salt) did in that solvent.

Several structural factors can effect the photochemistry and the spectroscopy of polymetric sensitizers. These include intramolecular and intermolecular energy transfer between immobilized dye residues,[16-21] association between dye molecules and photochemical manifestations of such associations,[22-25] and specific interactions between the dye matrix and singlet oxygen.[26,27]

In this work we outline the influence of the polymer support on the photochemical properties of an immobilized rose bengal and compare the polymer-bound dye when it is used under heterogeneous conditions to the same polymer-bound dye used either in a film or in solution.

Results and Discussion

The preparation and basic photochemical properties of poly-RB's in solution were described in our previous paper.[28] Poly-RB's are derived from poly(styrene-*co*-vinylbenzyl chloride) by nucleophilic displacement in polar, non-hydroxylic solvents. The extent of functionalization can be controlled by the ratio of the two reagents—polymer and dye. As elementary analysis showed, about 75% of rose bengal used in the synthesis is attached to the polymer

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