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Terminal and penultimate models of copolymerization in the styrene-acrylonitrile system in bulk according to UNIFAC

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UNIFAC—group contribution method for determination of local monomer concentrations and the simplex method for determination of reactivity ratios were used to describe the terminal and penultimate models of copolymerization in the styrene-acrylonitrile monomer system in bulk at 333.15 K. Results show that the procedure is applicable for prediction of the kinetic behaviour of the comonomer pair. Local monomer concentrations, true reactivity ratios, distribution coefficients K and the newly introduced parameter A, measuring deviation of the local concentration from the global concentration, were calculated. According to the results, the absolute value of the distribution coefficient K depends on the type of reactivity ratio but not on the monomer ratio in the feed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The styrene (M_1)-acrylonitrile (M_2) monomer system is one of the major examples found[1-8] to be much better described by the penultimate model[9] of copolymerization [equation (1)]:

$$n = \frac{d[M_1]}{d[M_2]} = \frac{1 + r_{21}\dfrac{[M_1]r_{11}[M_1] + [M_2]}{[M_2]r_{21}[M_1] + [M_2]}}{1 + r_{12}\dfrac{[M_2]r_{22}[M_2] + [M_1]}{[M_1]r_{12}[M_2] + [M_1]}} \quad (1)$$

then by the terminal model[10] [equation (2)]:

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} \quad (2)$$

where n represents the monomer ratio in copolymer, and $[M_1]$ and $[M_2]$ are the mole fractions of monomers M_1 and M_2, respectively. Parameters r_{11}, r_{22}, r_{21}, r_{12} and r_1, r_2 defined in the conventional way stand for the reactivity ratios of the monomers M_1 and M_2 in the penultimate model [equation (1)] and terminal model [equation (2)], respectively.

The monomer concentrations used in equations (1) and (2) should mean in fact monomer concentrations available for the growing radical. Harwood[11] remarked that these concentrations need not be the global monomer concentrations. In his 'bootstrap model' he introduced the distribution coefficient K, equal to the ratio between true ratio of monomers $[M_1]$ and $[M_2]$ in the neighbourhood of a growing polymer radical and a global monomer ratio [denoted in equation (3) by superscript 0]:

$$[M_1]/[M_2] = K[M_1^0]/[M_2^0] \quad (3)$$

Disregarding the partitioning effect of monomers leads one to evaluate the $r^t \cdot K$ product in conventional reactivity ratio

determinations equal to the apparent reactivity ratio and consider that the true reactivity ratio, r^t, has been determined.

Unfortunately, as far as we know, there is no publication on the theoretical or experimental determination of the absolute distribution coefficient K. Some attempts[8,12] have been made to relate the apparent reactivity ratios for solution copolymerization to bulk copolymerization as a reference state.

Although the 'bootstrap model' was proposed in order to explain the effects of solvent added to the polymerisation system, it is possible that the same differentiation of the monomer concentrations in the vicinity of the propagating radical (called true or local monomer concentrations) occurs as for the monomer mixture in bulk copolymerization.

In a recent paper[13] a two step procedure using UNIFAC - group contribution method has been proposed to calculate local monomer concentrations. The procedure was based on the fifth revision of UNIFAC and the extension according to Hansen *et al.*[14] and the modified Wilson equation[15]. For the terminal and the penultimate models of copolymerization, formulae were derived relating copolymer composition with local mole fractions and true reactivity ratios. These formulae enabled estimation of the true reactivity ratios for the styrene-methyl methacrylate monomer system in bulk at 313.15 K.

The aim of this paper is to prove the usefulness of the calculation procedure mentioned above to a monomer system displaying a significant penultimate effect. For both models of copolymerization, local monomer concentrations in the styrene-acrylonitrile monomer system in bulk are calculated; subsequently, the true reactivity ratios for the monomer system are estimated.

CALCULATION PROCEDURES

A detailed formal description of the calculation procedures has been given[13]. In terms of the group contribution method,

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UNIFAC, the styrene (M_1) and acrylonitrile (M_2) monomer molecules as well as two $(-M_1^\cdot \wedge -M_2^\cdot)$ and four $(-M_1M_1^\cdot, -M_1M_2^\cdot, -M_2M_1^\cdot, \wedge -M_2M_2^\cdot)$ reacting chain ends corresponding to the propagation steps in the terminal and the penultimate models of copolymerization, respectively, can be modelled by three different (sub)-groups: $CH_2{=}CH{-}$, aCH, and CH_2CHCN, where aC denotes an aromatic carbon. Accordingly, M_1 is modelled with one (sub)group $CH_2{=}CH{-}$ and six (sub)groups aCH. According to the fifth revision and extension of UNIFAC given by Hansen *et al.*[14], M_2 can be regarded as a one contribution group. For example, a growing macroradical end $PM_2M_1^\cdot$ consists of the following (sub)groups: one group CH_2CHCN, one (sub)group $CH_2{=}C{-}$ and six (sub)groups aCH.

Now taking the calculated local monomer concentrations for the terminal and penultimate models of copolymerization, corresponding formulae can be applied relating copolymer composition with local mole fractions and true reactivity ratios.

For the terminal model, equation (2) transforms into equation (4):

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_{12}](r_1^t[M_{11}] + [M_{21}])}{[M_{21}](r_2^t[M_{22}] + [M_{12}])} \quad (4)$$

where r_1^t and r_2^t stand for the true terminal reactivity ratios of monomers M_1 and M_2 respectively, and $[M_{11}]$, $[M_{12}]$ and $[M_{21}]$, $[M_{22}]$ are concentrations of monomers M_1 and M_2 in the immediate vicinity of the growing ends $-M_1^\cdot$ or $-M_2^\cdot$, respectively.

Analogously, for the penultimate model, equation (1) transforms in equation (5):

$$n = \frac{d[M_1]}{d[M_2]} = \frac{1 + r_{21}^t \dfrac{[M_{121}]r_{11}^t[M_{111}] + [M_{211}]}{[M_{211}]r_{21}^t[M_{121}] + [M_{221}]}}{1 + r_{12}^t \dfrac{[M_{212}]r_{22}^t[M_{222}] + [M_{122}]}{[M_{122}]r_{12}^t[M_{212}] + [M_{112}]}} \quad (5)$$

where r_{11}^t, $r_{21}^t \wedge r_{22}^t$, r_{12}^t stand for the true penultimate reactivity ratios of monomers M_1 and M_2, respectively, and M_{111}, M_{211}, M_{122}, M_{222}, M_{112}, M_{212}, M_{121}, M_{221} refer to the monomers M_1 and M_2 in the immediate vicinity of the corresponding ends of the growing macroradicals. For example, M_{212} refers to monomer M_2 in the nearest vicinity of the $-M_1M_2^\cdot$ end.

The reactivity ratios according to equations (4) and (5) were calculated using a modified Nelder-Mead[16] simplex method described already[17].

To characterize the deviation of the particular local concentration from the global concentration we introduced the parameter A equal to the Boltzman factor from the modified Wilson equation[15]. For example, for the terminal model the relationship between the particular local concentration and the global concentration is given by equation (6):

$$x_{ji}/x_j = x_{ji}(1 - A) + A \quad (6)$$

where x_j and x_{ji} $(i,j = 1,2)$ are the global and the local concentrations, respectively, and symbol x_{ji} means local concentration of molecule j in the cluster surrounding molecule of type i. A positive sign of the difference $(A - 1)$ means an excess in concentration of the monomer in the vicinity of the given growing macroradical end when compared with the global concentration of the monomer.

Monomer feed and copolymer composition data given by Hill *et al.*[4] for the styrene-acrylonitrile system in bulk at 333.15 K were used.

RESULTS AND DISCUSSION

In *Table 1* calculated local concentrations and corresponding values of parameter A in the terminal and penultimate models of copolymerization are given for the bulk styrene-acrylonitrile monomer system at 333.15 K. For comparison, we also show parameters A (for discrimination marked with star) for the styrene-methyl methacrylate system in bulk at

Table 1 Global mole fraction, χ_1, of styrene in feed for styrene (M_1)-acrylonitrile (M_2) system in bulk used by Hill *et al.*[4] and calculated corresponding local mole fractions in terminal, χ_i $(i,j = 1,2)$, and penultimate, χ_{ijk} $(i,j,k = 1,2)$, models of copolymerization at 333.15 K. For the convention used see the text. The A values correspond to the Boltzman factor from the modified Wilson equation[15] applied to the terminal and penultimate copolymerization model

Global	Terminal model				Penultimate model							
x_1	x_{11}	x_{22}	x_{12}	x_{21}	x_{111}	x_{222}	x_{122}	x_{211}	x_{112}	x_{221}	x_{121}	x_{212}
0.021	0.036	0.985	0.015	0.964	0.037	0.990	0.010	0.963	0.016	0.984	0.016	0.984
0.023	0.040	0.983	0.017	0.960	0.040	0.989	0.011	0.960	0.018	0.982	0.018	0.982
0.047	0.080	0.965	0.035	0.920	0.081	0.978	0.022	0.919	0.037	0.963	0.037	0.963
0.053	0.090	0.961	0.039	0.910	0.091	0.975	0.025	0.909	0.041	0.959	0.041	0.959
0.072	0.120	0.946	0.054	0.880	0.121	0.966	0.034	0.879	0.057	0.943	0.057	0.943
0.104	0.170	0.922	0.078	0.830	0.171	0.950	0.050	0.829	0.082	0.918	0.082	0.918
0.221	0.334	0.829	0.171	0.666	0.336	0.886	0.114	0.664	0.180	0.820	0.180	0.820
0.314	0.447	0.750	0.250	0.553	0.449	0.828	0.172	0.551	0.261	0.739	0.261	0.739
0.416	0.557	0.658	0.342	0.443	0.559	0.755	0.245	0.441	0.355	0.645	0.355	0.645
0.530	0.665	0.549	0.451	0.335	0.668	0.661	0.339	0.332	0.465	0.535	0.465	0.535
0.631	0.751	0.445	0.555	0.249	0.753	0.563	0.437	0.247	0.569	0.431	0.569	0.431
0.696	0.802	0.375	0.625	0.198	0.803	0.490	0.510	0.197	0.639	0.361	0.639	0.361
0.802	0.877	0.253	0.747	0.123	0.878	0.352	0.648	0.122	0.758	0.242	0.758	0.242
0.889	0.934	0.146	0.854	0.066	0.934	0.215	0.785	0.066	0.861	0.139	0.861	0.139
0.939	0.964	0.082	0.918	0.036	0.965	0.125	0.875	0.035	0.922	0.078	0.922	0.078
A	1.764	1.371	0.729	0.567	0.562	2.199	0.455	0.562	0.772	1.295	0.772	1.295
A^{*a}	1.109	1.082	0.925	0.903	1.490	1.059	0.945	0.671	1.342	0.769	1.301	0.745

a A^*: parameter A for the styrene (M_1)-methacrylate (M_2) monomer system in bulk at 313.15 given previously[13].

Table 2 Comparison of terminal and penultimate model reactivity ratios calculated using local monomer concentrations with those calculated using global concentrations for experimental data of Hill *et al.*[4]

	Apparently reactivity ratios			True reactivity ratios		Parameter K	
	Terminal model[a]	Penultimate model[b]		Terminal model[c]	Penultima model[d]	K_r^e	K_c^f
r_1	0.340		r_1'	0.193		1.76	1.76
r_2	0.054		r_2'	0.039		1.38	1.37
r_{11}		0.223	r_{11}'		0.137	1.63	1.78
r_{22}		0.038	r_{22}'		0.007	5.43	2.19
r_{21}		0.652	r_{21}'		1.057	0.62	0.77
r_{12}		0.098	r_{12}'		0.126	0.78	1.30
σ^g	0.0151	0.0048	σ	0.0151	0.0242		

[a] Using $r_1 = 0.3$ and $r_2 = 0.1$ as initial guesses for the least-squares (nlls) fit
[b] Using $r_{11} = r_{21} = r_1 = 0.3$ and $r_{22} = r_{12} = r_2 = 0.1$ as initial guesses for the nlls fit, results rounded to two digits given previously[17]
[c] Using terminal reactivity ratios calculated from global monomer concentrations as initial guesses for the nlls fit
[d] Using apparent penultimate reactivity ratios calculated from global monomer concentrations as initial guesses for the nlls fit
[e] The distribution coefficient K calculated as the ratio of the apparent reactivity ratio and true reactivity rations, $K_r = r/r_1$
[f] The distribution coefficient K calculated according to the equation (3) as the ratio of the local and global concentrations, for example, for the r_{21} and r_{21}' parameters, $K_c = (x_{121}/x_{221})/(x_1/(1-x_1))$
[g] Coefficient σ stands for the standard deviation in the reactivity ratio determination according to the method described previously[17]

313.15 K as calculated previously[13]. Comparison of both sets of the parameters, A and A^*, for the bulk styrene-acrylonitrile and styrene-methyl methacrylate monomer systems, respectively, clearly shows that, for the bulk styrene-acrylonitrile monomer system, deviation of the particular local concentrations from the global concentration is much greater than for the other system. These differences may be regarded as a measure of the difference between hetero- and homomolecular interactions (so called exchange energy) in both monomer systems. It is expected that the greater the difference the more probable is the penultimate effect in the monomer system.

Discussion of the corresponding distribution coefficients K presented in *Table 2* leads to some further remarks. The distribution coefficient K from equation (3) depends on the type of the reactivity ratio but not, as was speculated by Maxwell *et al.*[18], on the monomer ratio in the feed. The results may be regarded as theoretical evidence for one of Harwood's assumptions, later positively verified by Klumperman and Kraeger[8], namely, that the distribution coefficient K is influenced by the composition of a growing radical[11], and subsequently, by the copolymer composition[8]. This conclusion can be drawn despite the fact that, in the case of the penultimate model, the distribution coefficient K calculated as a ratio of the apparent reactivity ratio and true reactivity ratio, ($K_r = r/r^t$), differs from that calculated according to equation (3), (K_c), (*Table 2*). Several reasons can be responsible for this difference. First of all, as can be seen from *Table 2*, the smaller the apparent and true reactivity ratios are the greater is the difference between the two K values. Thus, any scattering in absolute values of the reactivity ratios results in considerable r/r^t variation. Therefore, the non-uniqueness[19] in determination of the penultimate reactivity ratios can also play a role in the determination of the distribution coefficient K. Note, that for the styrene-methyl methacrylate monomer system both distribution coefficients, K_r and K_c, had the same numerical value[13].

Copolymerization curves for both the terminal and the penultimate models, calculated according to the corresponding equations (1)–(2) and (4)–(5) from global and local concentrations, are shown in *Figure 1*. It shows that equations (4) and (5) used with the corresponding true reactivity ratios are well able to describe the experimental
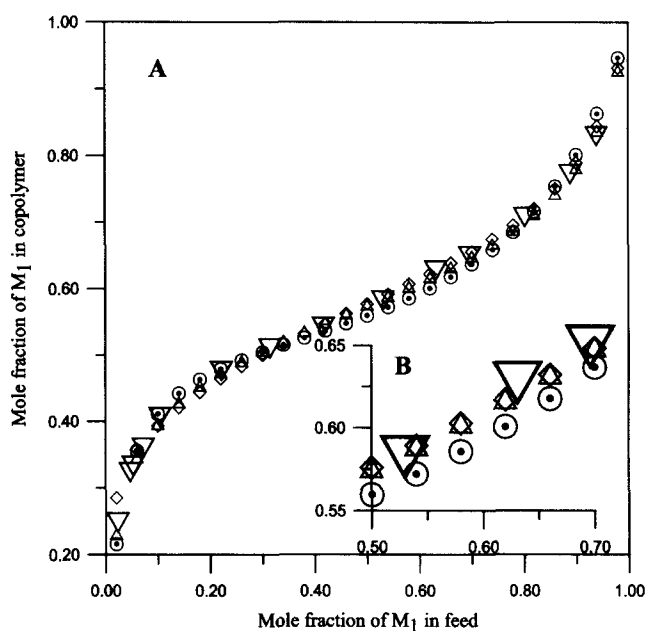

Figure 1 Copolymerization of styrene (M_1) and acrylonitrile (M_2). (∇): experimental data of Hill *et al.*[4]; (•) and (○) correspond to points in the terminal model of copolymerization calculated according to global and local monomer concentrations, [equation (2); $r_1 = 0.340$, $r_2 = 0.054$] and equation (4); $r_1' = 0.193$, $r_2' = 0.039$], respectively; (△) and (◇) correspond to points in the penultimate model of copolymerization calculated according to global and local monomer concentrations [equation (1); $r_{11} = 0.223$, $r_{22} = 0.038$, $r_{21} = 0.652$, $r_{12} = 0.098$] and [equation (5); $r_{11}' = 0.137$, $r_{22}' = 1.057$, $r_{12}' = 0.126$], respectively. All concentrations used in calculation are from *Table 1*. Part A is the general view; part B is an expanded section of A

composition copolymerization data. Moreover, as in the case of the conventional description of the kinetic models, the penultimate model using the local monomer concentrations and the corresponding true reactivity ratios appears to provide a better fit than the terminal model for the copolymer composition dependence on the monomer feed composition to the experimental data. Thus, it can be concluded that the already proposed two step procedure for the styrene-methyl methacrylate monomer system, using the UNIFAC—group contribution method, is applicable for prediction of the kinetic behaviour of a comonomer pair

with a penultimate effect like the styrene-acrylonitrile system.

CONCLUDING REMARKS

In this study, it has been shown that the UNIFAC—group contribution method could be used in theoretical determination of the local monomer concentrations in bulk for monomer systems which are described by the penultimate model of copolymerization. The calculation procedure associated with the simplex method for the reactivity ratio determination provides results which make allowance for the penultimate effect. Thus, it seems to be possible to predict, at least qualitatively, the probability of a penulti-mate effect in a given monomer system. According to the results, the absolute value of the distribution coefficient K depends on the type of reactivity ratio but not on the monomer ratio of feed.

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