ELSEVIER

Polymer 40 (1999) 6925–6932

polymer

Solvent effects on true terminal reactivity ratios for styrene—methyl methacrylate copolymerization system

A. Kaim*, P. Oracz

University of Warsaw, Faculty of Chemistry, ul. Pasteura 1, 02-093 Warsaw, Poland

Received 8 January 1999; received in revised form 4 February 1999; accepted 10 February 1999

Abstract

UNIFAC-group contribution method and the Wilson formula were used to study the solvent effects in the terminal model for radical copolymerization. Local monomer concentrations in the neighbourhood of growing polymer radicals were estimated in order to determine the true terminal reactivity ratios for the styrene—methyl methacrylate monomer system in bulk, and in benzene, toluene, benzyl alcohol and phenol. Coefficients of monomer partitioning, K_1 and K_2, in the vicinity of the growing macroradicals $–M_1\cdot$ and $–M_2\cdot$ were estimated. From the results, it was concluded that the solvent does influence the local monomer concentrations in the proximity of both growing macroradicals, $–M_1\cdot$ and $–M_2\cdot$, but not their ratios expressed as K_1^s and K_2^s, respectively. Constants K_1^s and K_2^s for solution copolymerization were equal to those for bulk copolymerization K_1^b and K_2^b, respectively. From the graphical analysis of the solvent effect, an increasing effect was suggested when changing the solvent from benzene < toluene < benzyl alcohol < phenol. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: UNIFAC-group contribution method; Wilson's local concentration concept; Radical copolymerization

1. Introduction

There are a few papers which present quantitative description of the solvent effect in radical copolymerization, according to the "bootstrap model" introduced by Harwood [1]. Recently, Klumperman and O'Driscoll [2] proposed a method for quantification of the distribution coefficient K introduced by Harwood to describe the ratio between local and global comonomer ratio:

$$[M_1]/[M_2] = K[M_1^0]/[M_2^0], \tag{1}$$

where $[M_1]$, $[M_2]$ and $[M_1^0]$, $[M_2^0]$ mean concentrations of monomers M_1 and M_2 in the neighbourhood of a growing polymer radical and global concentrations, respectively. For any copolymerization in a solvent, the usually determined reactivity ratios are apparent reactivity ratios, $r_i^s,\ (i = 1, 2)$:

$$r_1^s = r_1K^s, \tag{2}$$

$$r_2^s = r_2/K^s, \tag{3}$$

where r_i, $(i = 1,2)$, are the true reactivity ratios and K^s is the distribution coefficient as defined in Eq. (1) in the presence of solvent.

Because, up to now, determination of local monomer concentrations is experimentally not possible these authors did not focus on true reactivity ratios, but they related the apparent reactivity ratios to the ratios for copolymerization in bulk taken as a reference state. Although the monomer ratio at the site of propagation in bulk copolymerization probably differs from the global monomer ratio, they defined K for bulk to be unity ($K^b = 1$).

Hence, according to these authors, copolymerization in bulk is taken as a thermodynamic reference state making it possible to quantify the solvent effects in solution copolymerization.

When reactivity ratios were determined in bulk, Eqs. (2) and (3) transform to Eqs. (4) and (5):

$$r_1^s = r_1^bK^s, \tag{4}$$

$$r_2^s = r_2^b/K^s. \tag{5}$$

It follows that irrespective of the solvent employed

$$r_1^sr_2^s = r_1^br_2^b. \tag{6}$$

In the previous paper [3], the following model of copolymerization was constructed involving local monomer concentrations and true reactivity ratios. The growing end of a macroradical interacts with both monomers. There

---

* Corresponding author.

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00117-2

exists a competition between monomers for addition to the growing end proportional to their local mole fractions, which in turn are related to the differences in the interaction energies. In the model, we assumed that the monomer molecule to be added to the growing macroradical end is isolated from influences of remaining molecules. This assumption is equivalent to a model in which both monomers do not interact with themselves, but interact exclusively with the growing macroradical end. A copolymer composition Eq. (7) analogous to the Mayo–Lewis equation [4] was derived for the terminal model using true reactivity ratios, r_1, r_2 and local concentrations M_{ij} (i, j = 1,2) of the monomer M_1 and M_2, respectively:

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_{12}]}{[M_{21}]}\,\frac{(r_1[M_{11}] + [M_{21}])}{(r_2[M_{22}] + [M_{12}])}, \quad (7)$$

where M_{ij} stands for the local concentration of M_i in the cluster surrounding the monomer M_j. For determination of the true reactivity ratios, according to the formula (7), true monomer concentrations $[M_{11}]$, $[M_{12}]$ and $[M_{21}]$, $[M_{22}]$ of monomers M_1 and M_2 in the immediate vicinity of the corresponding growing ends $-M_1\cdot$ and $-M_2\cdot$ were needed. To this end, the Wilson formula was used relating the local mole fractions to the global values:

$$x_{ji}/x_{ii} = (x_j/x_i)\exp(-C_{ji}/RT), \quad (8)$$

where x_{ji} is the local mole fraction of molecule j in the cluster surrounding molecule i, x_i is the global mole fraction of molecule i, R is the gas constant, T is the temperature, and $C_{ji} = (g_{ji} - g_{ii})$ denotes the difference in the corresponding interaction energies. Using UNIFAC-group contribution method (in the way described previously [3]), C_{ji} parameters were estimated, and then the local concentrations and true reactivity ratios calculated according to Eqs. (8) and (7), respectively.

This model was expanded now to the influence of solvent and mutual "solvation" effects of both monomers, whereas the interactions between two species present in the reaction mixture are treated as independent from the remaining molecules.

The aim of the present paper is to provide a quantitative description of the solvent effect on free radical copolymerization according to the Wilson concept of binary mixtures. This approach makes it possible to quantify solvent effects in radical copolymerization described by the Mayo–Lewis model of copolymerization. This way, true reactivity ratios in bulk and in solution as well as the absolute distribution coefficients K's can be estimated.

For exemplification of the present approach, the solvent effect for the styrene—methyl methacrylate monomer system in bulk and in benzene, toluene, benzyl alcohol and phenol is discussed.

2. Theory

2.1. General concept of the monomer distribution at the propagation site

According to the "bootstrap model", the growing polymer radical governs its own environment. It means that the comonomer ratio available for the growing macroradical end depends on its terminal monomer unit. Thus, for the Mayo–Lewis model there is not one (as proposed by Harwood), but two different comonomer ratios available for the growing chain ending with $-M_1\cdot$ and $-M_2\cdot$, $[M_{11}]/[M_{21}]$ and $[M_{12}]/[M_{22}]$, respectively. Therefore, two different distribution coefficients K_1 and K_2 have to be considered:

$$[M_{11}]/[M_{21}] = K_1[M_1^0]/[M_2^0], \quad (9)$$

$$[M_{12}]/[M_{22}] = K_2[M_1^0]/[M_2^0]. \quad (10)$$

According to Eqs. (4) and (5), it follows for any solution polymerization that

$$r_1^s = r_1 K_1^s, \quad (11)$$

$$r_2^s = r_2/K_2^s, \quad (12)$$

where r_1^s, r_2^s and r_1, r_2 are apparent and true reactivity ratios, respectively, for solution copolymerization, K_1^s and K_2^s are solution distribution coefficients as defined in Eqs. (9) and (10), respectively.

As previously stated, the comonomer ratio available for the growing macroradical in bulk copolymerization can also differ from the global comonomer ratio. Thus, similar relations as for solution copolymerization (Eqs. (11) and (12)) can be defined for bulk copolymerization:

$$r_1^b = r_1 K_1^b, \quad (13)$$

$$r_2^b = r_2/K_2^b, \quad (14)$$

where the symbols for bulk copolymerization correspond to those for solution copolymerization.

From Eqs. (11) and (12), it follows that independent of the solvent employed

$$r_1^s r_2^s = \frac{K_1^s}{K_2^s} r_1 r_2. \quad (15)$$

From Eqs. (13) and (14) and for

$$K_1^b = K_1^s \quad (16)$$

$$K_2^b = K_2^s \quad (17)$$

Eq. (15) becomes Eq. (18):

$$r_1^s r_2^s = \frac{K_1}{K_2} r_1 r_2. \quad (18)$$

For $K_1 = K_2 = K$ and $r = r^b$, Eq. (18) reduces to Eq. (6)

Table 1
Dimensionless energetic parameters from Wilson relation (Eq. (8)), A_{jp}, for interactions between growing radical ends, monomers and solvents

Solvent	Dimensionless energetic parameters[a]					
	A_{12}	A_{13}	A_{42}	A_{43}	A_{1s}	A_{4s}
Benzene[b]	0.6499	0.9036	0.8378	0.5300	1.2582	1.0115
Toluene[c]	0.6429	0.9055	0.8368	0.5175	1.0718	0.5144
Benzyl alcohol[b]	0.6499	0.9036	0.8378	0.5300	0.1780	0.5342
Phenol[b]	0.6499	0.9036	0.8378	0.5300	0.1990	1.9261

[a] For the purpose of Table 1, dimensionless energetic parameters correspond to the following interacting pairs: A_{12}: macroradical styrene ending and methyl methacrylate A_{13}: macroradical styrene ending and styrene A_{42}: macroradical methyl methacrylate ending and methyl methacrylate A_{43}: macroradical methyl methacrylate ending and styrene A_{1s}: macroradical styrene ending and solvent A_{4s}: macroradical methyl methacrylate ending and solvent.

[b] Parameters calculated for 333.15 K; the temperature used by Ito and Otsu [10].

[c] Parameters calculated for 313.15 K; the temperature used by Fukuda et al. [9].

under the condition made by Klumperman and O'Driscoll [2] that for bulk, $K = 1$.

2.2. Calculation of the local monomer concentrations in solvent copolymerization

The local mole fraction of molecule j in the cluster surrounding the growing end of macroradical p can be expressed using Wilson relation (8):

$$x_{jp}/x_{pp} = (x_j/x_p)A_{jp} \tag{19}$$

where, for short, the exponential term in the local composition formula (in the vicinity of p) in Eq. (8) is denoted as $A_{jp} = \exp(-C_{jp}/RT)$ and all remaining symbols have the same meaning as previously. If 1 and 2 denote the corresponding monomers, s stands for solvent and p for growing macroradical, the following relations can be written as

$$x_{1p}/x_{pp} = (x_1/x_p)A_{1p} \tag{20}$$

$$x_{2p}/x_{pp} = (x_2/x_p)A_{2p} \tag{21}$$

$$x_{sp}/x_{pp} = (x_s/x_p)A_{sp}. \tag{22}$$

Both local and global mole fractions in Eqs. (20)–(22) give unity

$$x_{pp} + x_{1p} + x_{2p} + x_{sp} = 1 \tag{23}$$

$$x_1 + x_2 + x_s + x_p = 1. \tag{24}$$

Substitution of Eqs. (20)–(22) in Eq. (24) gives (after simple rearrangements and assuming that $x_p \approx 0$ when compared to the monomers and solvent concentrations) formulae (25) for mole fractions of all species i in the

Table 2
Global mole fractions of styrene (x_1) and methyl methacrylate (x_2) in feed in copolymerization in bulk, toluene (data by Fukuda et al. [8,9], respectively), benzene, benzyl alcohol, phenol (data by Ito and Otsu [10]) and corresponding local mole fractions in terminal model of copolymerization calculated according to UNIFAC. For the convention see the text

Solvent	Global mole fractions of monomers in feed		Local mole fractions of monomers in feed			
	x_1	x_2	x_{21}	x_{11}	x_{22}	x_{12}
Bulk[a]	0.046	0.954	0.936	0.064	0.971	0.029
	0.096	0.904	0.870	0.130	0.938	0.062
	0.121	0.879	0.838	0.162	0.922	0.078
	0.194	0.806	0.747	0.253	0.870	0.130
	0.210	0.790	0.728	0.272	0.859	0.141
	0.241	0.759	0.691	0.309	0.836	0.164
	0.319	0.681	0.603	0.397	0.775	0.225
	0.422	0.578	0.493	0.507	0.689	0.311
	0.474	0.526	0.441	0.559	0.642	0.358
	0.592	0.408	0.329	0.671	0.527	0.473
	0.692	0.308	0.240	0.760	0.418	0.582
	0.702	0.298	0.232	0.768	0.407	0.593
	0.756	0.244	0.186	0.814	0.343	0.657
	0.774	0.226	0.172	0.828	0.321	0.679
	0.786	0.214	0.162	0.838	0.306	0.694
	0.832	0.168	0.125	0.875	0.246	0.754
	0.891	0.109	0.080	0.920	0.165	0.835
	0.944	0.056	0.040	0.960	0.088	0.912
Benzene	0.048	0.434	0.289	0.044	0.398	0.028
	0.095	0.382	0.250	0.087	0.356	0.056
	0.142	0.330	0.213	0.127	0.312	0.085
	0.186	0.281	0.179	0.165	0.270	0.113
	0.230	0.231	0.145	0.201	0.225	0.142
	0.274	0.183	0.113	0.236	0.181	0.171
	0.316	0.136	0.083	0.269	0.136	0.200
	0.358	0.089	0.054	0.300	0.091	0.230
Toluene	0.022	0.459	0.339	0.023	0.580	0.017
	0.080	0.394	0.285	0.081	0.514	0.065
	0.091	0.382	0.275	0.092	0.501	0.074
	0.175	0.288	0.201	0.172	0.396	0.149
	0.208	0.252	0.174	0.203	0.354	0.181
	0.209	0.251	0.174	0.204	0.352	0.181
	0.268	0.185	0.125	0.256	0.269	0.241
	0.298	0.152	0.102	0.282	0.225	0.273
	0.353	0.091	0.060	0.328	0.140	0.335
	0.396	0.043	0.028	0.363	0.068	0.387
Benzyl alcohol	0.051	0.468	0.698	0.106	0.580	0.040
	0.103	0.411	0.598	0.208	0.523	0.083
	0.153	0.356	0.506	0.303	0.465	0.126
	0.201	0.303	0.422	0.389	0.406	0.170
	0.249	0.250	0.341	0.472	0.344	0.217
	0.296	0.198	0.265	0.550	0.280	0.265
	0.342	0.147	0.193	0.624	0.213	0.314
	0.387	0.097	0.125	0.693	0.145	0.365
	0.432	0.047	0.059	0.760	0.072	0.419
Phenol	0.140	0.327	0.477	0.284	0.199	0.054
	0.185	0.278	0.397	0.368	0.171	0.072
	0.206	0.255	0.361	0.405	0.157	0.080
	0.228	0.229	0.322	0.445	0.141	0.089
	0.272	0.181	0.249	0.520	0.112	0.107
	0.318	0.130	0.175	0.597	0.081	0.126

[a] Due to some changes in the modelling of the styrene and methyl methacrylate radical molecules, local mole fractions of monomers in feed differ slightly from the data published earlier [3].

Table 3

Apparent and true terminal model reactivity ratios for the free-radical copolymerization of styrene (r_1) with methyl methacrylate (r_2) calculated according to the Nelder and Mead simplex method [6], and corresponding distribution coefficients K_1 and K_2 calculated from local monomer concentrations and from true and apparent reactivity ratios

Solvent		Apparent reactivity ratios,[a] r_i^b or r_i^s ($i = 1,2$)	True reactivity ratios,[b] r_i ($i = 1,2$)	Distribution coefficient[c] K_i ($i = 1,2$)	Distribution coefficient[d] K_i ($i = 1,2$)
Bulk[e]	r_1	0.550[f]	0.390[g]	1.408	1.410
	r_2	0.482	0.298	0.618	0.618
	σ[h]	0.01113	0.01113		
Benzene[i]	r_1	0.589	0.424	1.390	1.389
	r_2	0.481	0.304	0.633	0.632
	σ	0.00344	0.00344		
Toluene[j]	r_1	0.535	0.380	1.408	1.408
	r_2	0.392	0.243	0.618	0.620
	σ	0.00650	0.00652		
Benzyl alcohol[i]	r_1	0.441	0.317	1.390	1.391
	r_2	0.406	0.256	0.633	0.630
	σ	0.00625	0.00625		
Phenol[i]	r_1	0.347	0.250	1.390	1.388
	r_2	0.367	0.232	0.633	0.632
	σ	0.00470	0.00470		

[a] Calculated with global monomer concentrations.

[b] Calculated with local monomer concentrations.

[c] Distribution coefficient K_i ($i = 1,2$) from local monomer concentrations calculated according to Eqs. (9) and (10).

[d] Distribution coefficient K_i ($i = 1,2$) calculated from true and apparent reactivity ratios according to Eqs. (13) and (14).

[e] Calculated using experimental data at 313.15 K of Fukuda et al. [8].

[f] Results given previously [3].

[g] When molecule j and i in the Wilson formula Eq. (7) are for simplification reduced to intact monomer molecules (growing copolymer ends are not constructed as described before), true reactivity ratios, r_1 and r_2, are 0.496 and 0.444, respectively [7].

[h] Standard deviation calculated as $\sigma = \sqrt{\sum_{i=1}^{n}[F_i(\text{exptl}) - F_i(\text{calc})]^2/(n-2)}$, where F is the fraction of monomer M_1 in the copolymer, n, the number of experimental points and 2, the number of r-parameters.

[i] Calculated using experimental data at 333.15 K of Ito and Otsu [10].

[j] Calculated using experimental data at 313.15 K of Fukuda et al. [9].

vicinity of the growing end of macroradical p:

$$x_{ip} = \frac{x_i A_{ip}}{x_i A_{ip} + x_i A_{ip} + x_i A_{ip}}, \qquad (i = 1, 2, s). \tag{25}$$

To calculate the local mole fractions using this formula, the binary interaction parameters, C_{jp}, have to be estimated.[1] According to the group contribution method—UNIFAC [5], both monomers (styrene and methyl methacrylate), solvents (like benzene, toluene, phenol and benzyl alcohol) as well as the two growing macroradical ends can be modelled by twelve different (sub)groups:

$-CH_3$, $-CH_2-$, $>C<$, $CH_2{=}CH-$, $CH_2{=}C<$, aCH, aC, $aCCH_3$, aCCH$<$, $aCCH_2-$, $-OH$, aCOH, COO–, where aC denotes an aromatic carbon. From this, M_1 is modelled with one (sub)group $CH_2{=}CH-$, five (sub)groups aCH and one aC. Monomer molecule M_2 is assembled from the following (sub)groups: two $-CH_3$, one $CH_2{=}C<$ and one –COO–. A growing macroradical styrene end can be constructed with one (sub)group $-CH_2-$, five (sub)groups aCH and one group aCCH$<$. A growing macroradical ester end can be constructed with two (sub)groups $-CH_3$, one (sub)group $-CH_2-$, one group –COO– and one (sub)group $>C<$. Benzene consists of six (sub)groups aCH, toluene of five (sub)groups aCH and one (sub)group $aCCH_3$, phenol of five (sub)groups aCH and one group of aCOH, and benzyl alcohol five (sub)groups of aCH, one group of $aCCH_2-$ and one group –OH.

The calculation procedure for reactivity ratios using the non-linear least-squares (nlls) fit based on the Nelder and Mead [6] simplex method has been described previously [7].

For the present work, experimental data of Fukuda et al. at 313.15 K for copolymerization in bulk [8] and toluene [9], as well as of Ito and Otsu [10] at 333.15 K in benzene, benzyl alcohol and phenol have been considered. The choice of experimental data available in literature was restricted to

---

[1] Support in application of the UNIFAC-group contribution method can be available on request.

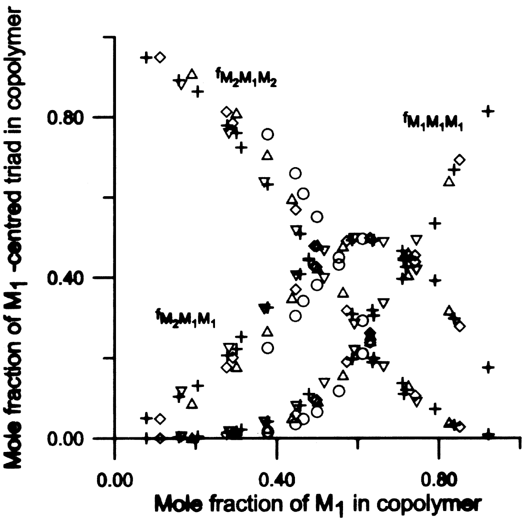

Fig. 1. Mole fraction of styrene (M_1) centred triads $f_{M_1M_1M_1}$, $f_{M_2M_1M_1}$ and $f_{M_2M_1M_2}$ versus mole fraction of M_1 in the styrene—methyl methacrylate copolymer: (+) bulk [8], (▽) benzene [10], (◇) toluene [9], (△) benzyl alcohol [10], (○) phenol [10]. Points obtained with the procedure given by Harwood [1] were the same for apparent and true reactivity ratios (Table 3) used for calculations.

those containing information on global monomer and solvent concentrations during copolymerization. These data are necessary to calculate the local concentrations of monomer M_1 and M_2 and subsequently, the distribution coefficients K_1^b, K_2^b and K_1^s, K_2^s as defined before.

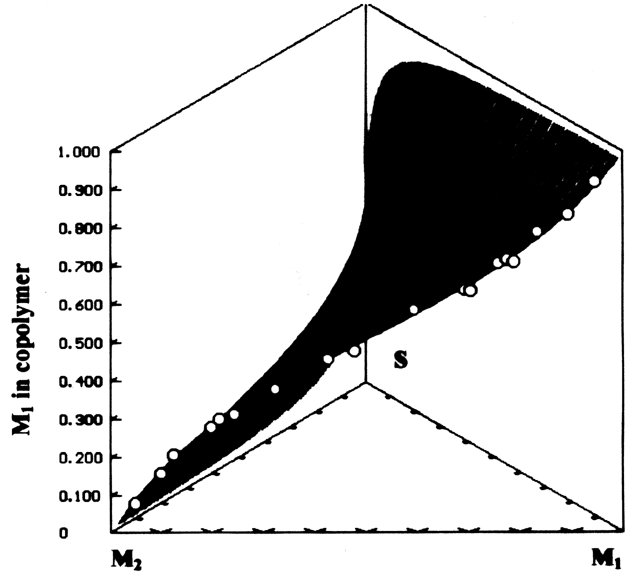

Fig. 2. Effect of dilution with the hypothetical inert solvent S on composition of the bulk styrene (M_1) with methyl methacrylate (M_2) copolymer. For construction of surface *F*, showing the dependence of the copolymer composition (M_1 in copolymer) on M_1, M_2 and S concentrations in feed, see the text. Points refer to the experimental data of Fukuda et al. [8] for bulk copolymerization (the concentration of solvent S, x_S, equals zero). Note that for clarity of presentation, drawings were prepared for mole fractions of monomers and solvent greater than 0.02.

3. Results and discussion

Dimensionless energetic parameters C_{ji} from the Wilson relation (Eq. (8)) for interactions between growing radical ends, monomers and solvents calculated with UNIFAC-group contribution method are presented in Table 1.

Local concentrations of monomer M_1 and M_2 in the vicinity of the growing ends $–M_1\cdot$ and $–M_2\cdot$ were estimated from Eq. (25) (Table 2). Subsequently, the true terminal reactivity ratios, r_1 and r_2, for the styrene—methyl methacrylate system in benzene, benzyl alcohol, phenol (at 333.15 K), bulk and toluene (at 313.15 K) were determined according to Eq. (7). For comparison, apparent reactivity ratios, r_1^b, r_2^b and r_1^s, r_2^s, were calculated using the original Mayo–Lewis equation. True and apparent reactivity ratios, as well as distribution coefficients calculated from local monomer concentrations (Eqs. (9) and (10)) and from true and apparent reactivity ratios ((11), (12), (13), (14)) are presented in Table 3.

As shown in Table 3, both the distribution coefficients, K_1 and K_2, calculated from local monomer concentrations and reactivity ratios are almost identical. Influence of the polymerization temperature on the distribution coefficients reflects the contribution of the parameter in the Wilson formula (8). From the data given in Tables 2 and 3, it can be concluded that the solvent does influence the local monomer concentrations in the proximity of both the growing macroradicals, $–M_1\cdot$ and $–M_2\cdot$, but not their ratio expressed for the growing ends as K_1^s and K_2^s, respectively. Moreover, constants K_1^s and K_2^s for solution copolymerization equals those for bulk copolymerization K_1^b and K_2^b, respectively. Both these conclusions make more understandable the observation made by Harwood [1]; why for the same copolymer composition, independent of the solvent (or bulk) used for copolymerization, the same microstructure of copolymers is observed. A direct comparison of the obtained distribution coefficients with those given by Klumperman and O'Driscoll [2] is not possible for several reasons. First of all, these authors used only one distribution coefficient K^s defined in Eq. (1) and related it to the two reactivity ratios as shown in Eqs. (2) and (3). This distribution coefficient K^s does not have any simple relation with distribution coefficients K_1^s and K_2^s defined in Eqs. (9) and (10) and correlated with reactivity ratios as presented in Eqs. (11) and (12). From the point of view of the present model, the distribution coefficient K^s is probably some averaged value from K_1^s and K_2^s. Further, as mentioned before, the distribution coefficients K^s estimated by these authors for the styrene—methyl methacrylate system in benzene, chlorobenzene and benzonitrile are related to the copolymerization in bulk taken as a reference state ($K^b = 1$). Thus, the authors calculated the distribution coefficients K^s from the apparent reactivity ratios for both bulk and solution polymerization. The comparison of the distribution coefficients K^s for the styrene—methyl methacrylate system following the procedure by Klumperman and O'Driscoll

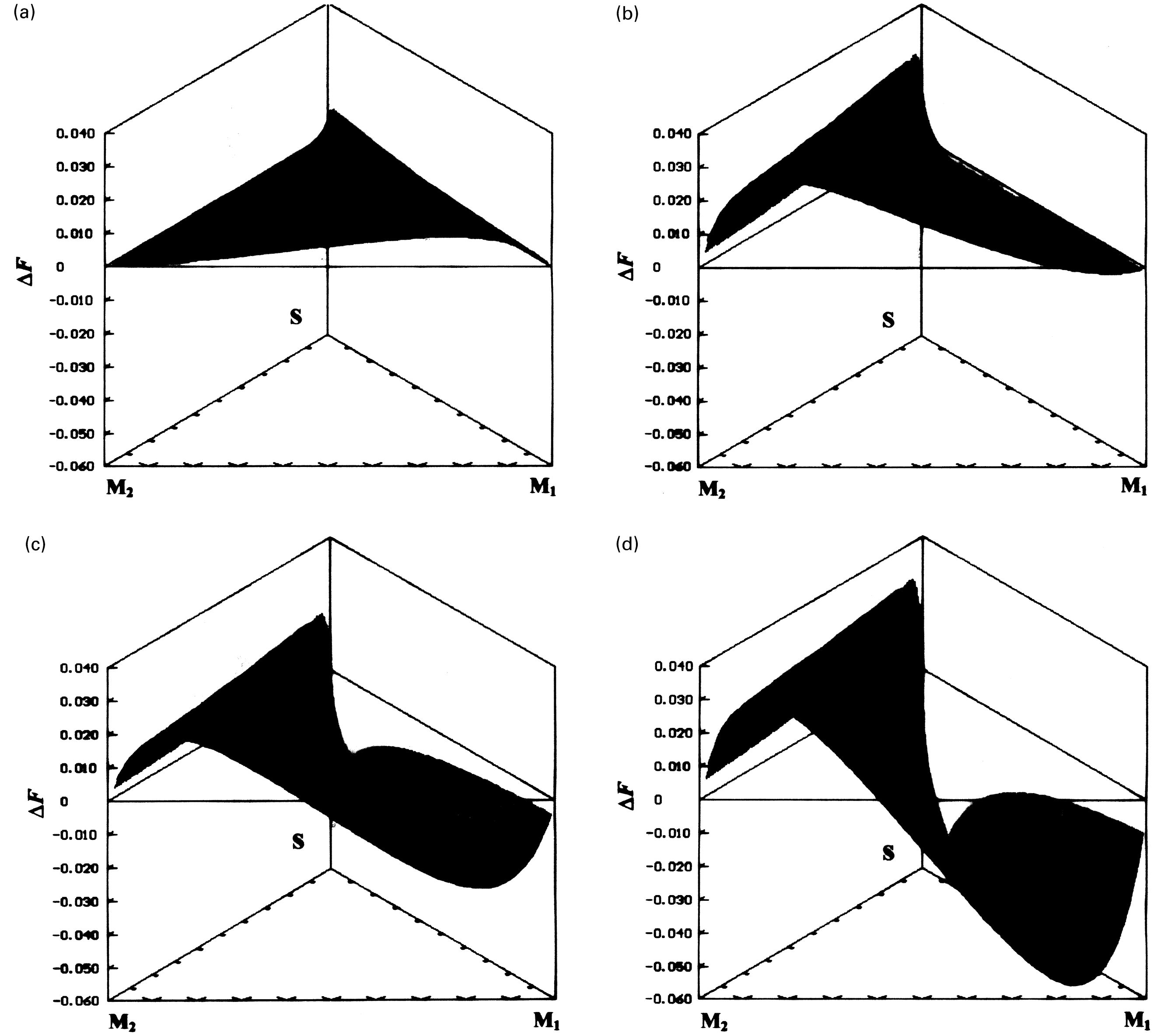

Fig. 3. Solvent effects on composition of styrene (M_1) with methyl methacrylate (M_2) copolymer is presented. For construction of the difference ΔF between surface F corresponding to the monomer pair dissolved in a real solvent (a), (b), (c), (d) and surface F for the hypothetical inert solvent S, see the text: (a) benzene (data by Ito and Otsu [10]), (b) toluene (data by Fukuda et al. [9]), (c) benzyl alcohol (data by Ito and Otsu [10]), (d) phenol (data by Ito and Otsu [10]). See also the note in the caption of Fig. 2.

[2], i.e. from apparent reactivity ratios, can be performed only for polymerization in benzene (Table 1). The calculated distribution coefficients K^s are equal to 0.934 (K from r_1) and 0.998 (K from r_2). The values given by these authors are 0.93 and 0.95, respectively. To verify whether with true reactivity ratios a proper microstructure of copolymer is still achieved, both true and apparent reactivity ratios were considered to estimate the styrene (M_1)-centred triad sequence distribution according to the procedure proposed by Harwood [1]. (M_1)-centred triad fractions, $f_{M_1M_1M_1}$, $f_{M_2M_1M_1}$ and $f_{M_2M_1M_2}$, calculated from the terminal model versus M_1 in styrene—methyl methacrylate copolymers obtained in bulk, benzene, toluene, benzyl alcohol and phenol are presented in Fig. 1. Except for some deviations for benzyl alcohol and phenol discussed earlier [11], arrangement of the points is conformable with the "bootstrap model". As shown in Fig. 1, both the true and apparent reactivity ratios lead to the same microstructure of the copolymers obtained in the discussed solvents. It allows us to conclude the equivalency in description of the microstructure of the copolymer with both, true and apparent, reactivity ratios. Thus, there is equivalence in the microstructure description of the current model relating the true reactivity ratios with local monomer concentrations and a

classical approach relating apparent reactivity ratios with global monomer concentrations. Simultaneously, this result presents some kind of positive verification of the local monomer concentration concept presented herein.

As the coefficients of monomer partitioning K_1 and K_2 do not depend on the solvent but on the monomer pair, these parameters cannot be used for comparison of the induced solvent effect. For the following purpose, graphical presentation of the solvent effects can be adopted. All copolymer compositions corresponding to local concentrations calculated in the following were performed according to Eq. (7). First, an effect of dilution with a hypothetical inert solvent on the composition of the bulk copolymer was considered. Local concentrations necessary for the calculation were estimated with the assumption that the interaction energy differences C_{1s}, C_{2s} and C_{sp} are zero (Fig. 2). Next, the copolymer compositions for solution copolymerization in real solvents like benzene, toluene, benzyl alcohol and phenol were calculated according to Eq. (7) (now however, C_{1s}, C_{2s} and C_{sp} are not equal to zero and can be calculated according to the UNIFAC-group contribution method as described before). For both a hypothetical inert solvent and a real solvent, the copolymer composition was calculated for 50 molar ratios of M_1 (molar ratio from 0 to 1, step 0.02). Note, that for $x_s = 0$ a conventional copolymerization diagram is obtained. For example, points in Fig. 2 correspond to experimental results for bulk copolymerization of the styrene—methyl methacrylate system [8]. An effect of benzene, toluene, benzyl alcohol and phenol on the composition of the copolymer can be expressed as a difference between the copolymer composition for solution copolymerization and that for copolymerization in bulk (Fig. 3). It appears from Fig. 3 that the solvent effect increases in the following order: benzene < toluene < benzyl alcohol < phenol.

We tried to explain this order in the same way as Klumperman and O'Driscoll [2] for copolymerization [12] of styrene with methyl methacrylate in bulk, benzene, chlorobenzene and nitrobenzene. These authors supported the idea put forward by Russo [13] that the variation in the reactivity ratio correlates with the polarity of the solvent. This explanation fails in our case. Permanent dipole moments for benzene, toluene, benzyl alcohol and phenol measured under comparable conditions are, 0 [14], 0.36 [14], 1.67 [15] and 1.45 Debye [15], respectively. Thus, one could expect the solvent effect for benzyl alcohol to be greater than that for phenol. However, this is not so in our case as shown in Fig. 3. Hence, at least for the discussed solvents, polarity of the solvent is probably not the only parameter responsible for solvent effects during the radical copolymerization. The influence of the solvent on radical copolymerization presents certainly a more complex problem. More than twenty years ago, a long list of the factors discussed in the literature was given by Bontà et al. [16]. Recently, it was claimed [17] that a solvent influences the Arrhenius parameters for styrene and methyl methacrylate propagation rate constants in an univocal way. Among the reported solvents, benzyl alcohol had an exceptionally great effect on the methyl methacrylate propagation rate. Additionally, O'Driscoll et al. [18] reported that tacticity of poly(MMA) formed in the presence of benzyl alcohol increased with the alcohol concentration in the polymerization system. This result is interpreted as supporting the hypothesis that benzyl alcohol forms a strong complex with the radical chain ends terminating with methyl methacrylate and a week complex with those terminating with styrene. It recalls the result discovered earlier [11] that the microstructure of the styrene—methyl methacrylate copolymers obtained in solvents containing a labile hydrogen atom, like benzyl alcohol and phenol, shows deviation with respect to the "bootstrap model". This effect was found to be stronger for phenol within agreement with the present results that the solvent effects were greater for phenol than for benzyl alcohol. Ito and Otsu [10] suggest that the polarized structure ($>C^+–O^-$) of methyl methacrylate becomes more important, enhancing its reactivity as the solvent used is more protic.

4. Conclusions

From the present model assuming that the comonomer ratio available for the growing macroradical end depends on its terminal monomer unit, it follows that two different distribution coefficients K_1 and K_2 have to be considered. Taken together, both the group contribution method (UNIFAC) and the local monomer concentrations concept, applied for solution copolymerization offer a chance to estimate the distribution coefficients K_1 and K_2 in the vicinity of the growing macroradicals $–M_1\cdot$ and $–M_2\cdot$, respectively. From the results obtained according to the developed model, it is concluded that the solvent influences the local monomer concentrations in the proximity of both growing macroradicals but not their ratio. Distribution coefficients for bulk K_1^b, K_2^b and solution copolymerization K_1^s, K_2^s, are respectively equal. Thus, copolymerization in bulk can be regarded as a variant of solution copolymerization. Increasing solvent effects when changing from benzene < toluene < benzyl alcohol < phenol suggest that both polarity of solvent and hydrogen-bonding are the factors responsible for the solvent effects during radical copolymerization.

Acknowledgements

This work was supported with 120-501/68-BW-1418/18/98 and BST/592/16/98 by the Faculty of Chemistry, University of Warsaw.

References

[1] Harwood HJ. Makromol Chem, Macromol Symp 1987;10/11:331.
[2] Klumperman B, O'Driscoll KF. Polymer 1993;34:1032.
[3] Kaim A, Oracz P. Macromol Theory Simul 1998;7:97.

[4] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594.

[5] Hansen HK, Rasmussen P, Fredenslund A, Schiller M, Gmehling J. Ind Eng Chem Res 1991;30:2352.

[6] Nelder OA, Mead R. Comput J 1964;7:308.

[7] Kaim A, Oracz P. Polymer 1997;38:2221.

[8] Fukuda T, Ma Y-D, Inagaki H. Macromolecules 1985;18:17.

[9] Fukuda T, Kubo K, Ma Y-D, Inagaki H. Polymer J 1987;19:523.

[10] Ito T, Otsu T. J Macromol Sci-Chem 1969;A3:197.

[11] Kaim A. J Macromol Sci-Pure Appl Chem 1996;A33(11):1711.

[12] San Román J, Madruga EL, Del Puerto MA. Angew Makromol Chem 1980;86:1.

[13] Russo S. Polymer 1975;16:429.

[14] Becker R, Freedman K. J Am Chem Soc 1985;107:1477.

[15] Boud AH, Cleverdon D, Collins GB, Smith JW. J Chem Soc 1955:3793.

[16] Bontà G, Gallo BM, Russo S. Polymer 1975;16:429.

[17] Zammit MD, Davis TP, Willett GD, O'Driscoll KF. J Polym Sci Polym Chem Ed 1997;35:2311.

[18] O'Driscoll KF, Monteiro MJ, Klumperman B. J Polym Sci Polym Chem Ed 1997;35:515.