Solvent effects on the copolymerization of styrene with maleic anhydride: determination of apparent reactivity ratios from the penultimate unit model

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SOLVENT EFFECTS ON THE COPOLYMERIZATION OF STYRENE WITH MALEIC ANHYDRIDE: DETERMINATION OF APPARENT REACTIVITY RATIOS FROM THE PENULTIMATE UNIT MODEL

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Abstract—A method for optimization of monomer feed composition to obtain the most accurate reactivity ratios has been described by Tidwell and Mortimer. The proposed method is more generally applicable than for use with the Mayo–Lewis model and copolymer composition vs monomer feed composition data. By means of a simulated example involving the penultimate unit models the effect of experimental design in the determination of reactivity ratios is clearly demonstrated. The same technique is adapted to the copolymerization of styrene with maleic anhydride. Apparent reactivity ratios are obtained for polymerization in toluene, butanone and *N,N'*-dimethylformamide. There appears to be a significant solvent effect. This paper provides an indication that the highest obtainable accuracy of apparent reactivity ratios depends on the values of the reactivity ratios themselves.

Interpretation of the experimental results in terms of the bootstrap model leads to the conclusion that there is no dependence of monomer sequence distribution vs copolymer composition on the solvent. Quantitative interpretation is hampered most probably by the absence of maleic anhydride homopolymerization.

INTRODUCTION

Solvents appear to affect the apparent reactivity ratios in radical copolymerization. The extent is strongly dependent on the nature of the monomers and the solvents involved. Numerous explanations of the observed phenomena have been given. A few years ago it was discovered that, although the apparent reactivity ratios are influenced by the solvent, the reaction medium does not influence the conditional probabilities of the chain growth. Harwood demonstrated [1] on four examples that significant solvent effects on the copolymer composition vs monomer feed curves did not result in any effect on the monomer sequence (e.g. triad distribution) vs copolymer composition curves. The four examples in Harwood's publication consist of comonomers with relatively large differences in polarity. In a recent communication, Davis showed that this so-called "bootstrap effect" could also explain the observed solvent effects on styrene with methyl methacrylate copolymerization. [2] A method for quantification of the bootstrap effect was proposed by Klumperman and O'Driscoll [3]. In their publication, copolymerizations of styrene with methyl methacrylate and with maleic anhydride were used as examples. In a recent publication Klumperman and Kraeger [4] modified the proposed method to account for the variation of the distribution coefficient with copolymer composition. This distribution coefficient is defined to describe the ratio between comonomer

ratio at the site of propagation and global comonomer ratio (i.e. mean comonomer ratio over the entire reaction vessel). In the latter publication, the copolymerization between styrene and acrylonitrile was used as an example of a system that obeys the penultimate unit model, as was shown by two independent techniques [5, 6].

The determination of accurate values of the apparent reactivity ratios in radical copolymerization has been the subject of many studies. A generally accepted fact is that, once experimental data has been gathered, the use of a non-linear least squares (NLLS) method provides the most accurate values of the reactivity ratios [7–9].

Furthermore it appears to be of great importance to perform the right experiments. This means that with a fixed number of experiments, the accuracy of the reactivity ratios is strongly influenced by the comonomer feeds at which experiments are performed. This feature was recognized a number of years ago for the Mayo–Lewis model and the determination of reactivity ratios from copolymer composition vs monomer feed data, by Tidwell and Mortimer [9]. The method proposed by them to optimize the experiments is more generally applicable. Using the same technique, which will be outlined below, optimal experiments can be developed to evaluate any copolymerization model from any type of experimental data.

In this paper a simulated system will be used to show the effect of optimal experiments for the determination of reactivity ratios from the penultimate unit model. Afterwards, the approach will be used to

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obtain apparent reactivity ratios for the copolymerization of styrene with maleic anhydride in three different solvents (toluene, butanone and N,N-dimethylformamide).

PLANNING OF EXPERIMENTS

That randomly distributed comonomer feed ratios in general do not lead to the most accurate reactivity ratios has been shown before [9]. Tidwell and Mortimer provided a boundary condition to which a joint confidence interval should match. As they say "those experimental conditions which generate circular joint confidence limits (or elliptical confidence limits with the axes of the figure parallel to the coordinate axes in an orthogonal r_1, r_2 space) are preferred".

It has been shown that minimization of the area of the joint confidence intervals can be achieved by maximizing the modulus of the determinant D , where

$$D = \begin{vmatrix} \frac{\partial G(M_{11}; r_{ij})}{\partial r_{11}} & \frac{\partial G(M_{11}; r_{ij})}{\partial r_{21}} & \frac{\partial G(M_{11}; r_{ij})}{\partial r_{12}} & \frac{\partial G(M_{11}; r_{ij})}{\partial r_{22}} \\ \frac{\partial G(M_{12}; r_{ij})}{\partial r_{11}} & \frac{\partial G(M_{12}; r_{ij})}{\partial r_{21}} & \frac{\partial G(M_{12}; r_{ij})}{\partial r_{12}} & \frac{\partial G(M_{12}; r_{ij})}{\partial r_{22}} \\ \frac{\partial G(M_{13}; r_{ij})}{\partial r_{11}} & \frac{\partial G(M_{13}; r_{ij})}{\partial r_{21}} & \frac{\partial G(M_{13}; r_{ij})}{\partial r_{12}} & \frac{\partial G(M_{13}; r_{ij})}{\partial r_{22}} \\ \frac{\partial G(M_{14}; r_{ij})}{\partial r_{11}} & \frac{\partial G(M_{14}; r_{ij})}{\partial r_{21}} & \frac{\partial G(M_{14}; r_{ij})}{\partial r_{12}} & \frac{\partial G(M_{14}; r_{ij})}{\partial r_{22}} \end{vmatrix}$$

G is the quantity which will be measured (e.g. copolymer composition) and r_{ij} are the apparent reactivity ratios, in this case for the penultimate unit model. When G describes one of the triads, the determinant reduces to $[2 \times 2]$ size. This is obvious from the mathematical description of the triad fractions (e.g. F_{111} is determined by r_{11} and r_{21} in the penultimate unit model).

For the maximization of the modulus of this determinant, the best available estimates of these apparent reactivity ratios should be applied. They can be determined from preliminary experiments. Maximization of the modulus of this $[4 \times 4]$ determinant is done numerically by starting from an arbitrarily chosen point in the four dimensional space $\{M_{11}, M_{12}, M_{13}, M_{14}\}$ and moving through this space on the basis of steepest increase of the modulus. The step size is decreased when the maximum is approached to a certain degree, so that the maximum can be determined with the highest precision. In principle,

more than one maximum could occur in this four dimensional space, so that the starting point of the calculation could play a significant role. During the calculations so far, this has never been observed.

SIMULATION OF REACTIVITY RATIO DETERMINATION

A fictive system which obeys the penultimate unit model with the following apparent reactivity ratios is considered:

$$r_{11} = 0.100$$

$$r_{21} = 0.300$$

$$r_{12} = 0.200$$

$$r_{22} = 0.400.$$

Two data sets are simulated by computer. One set consists of four monomer feeds equally distributed over the entire monomer feed range ($f_1 = 0.2, 0.4, 0.6$

and 0.8). The second set is obtained by the procedure as described above. The values for f_1 in this case are 0.066, 0.261, 0.741 and 0.971. Copolymer composition is calculated using the penultimate unit model with the above mentioned reactivity ratios. The occurrence of composition drift is not invoked in the simulations. For each comonomer feed four copolymer compositions are calculated, to simulate a 4-fold experiment. Errors are introduced by a random number generator. A maximum relative error of 0.01 is allowed for the monomer feed, while a maximum absolute error of 0.03 is allowed for copolymer composition. From the data sets obtained in this way, reactivity ratios are estimated using a non-linear least squares procedure [10]. The estimated values are listed in Table 1.

When the estimated values are compared with the true values, it is easily recognized that a significant deviation occurs for the first set, while the second set yields a fairly good agreement. The accuracy of the estimates is represented graphically in Figs 1 and 2, where the 95% joint confidence intervals are plotted. The confidence intervals are calculated according to a method described by Hautus *et al.* [11]. The main difference between the two estimates in Fig. 1 (r_{11} and r_{21}) is the surface area of the confidence interval, whereas the main differences in Fig. 2 (r_{22} and r_{12}) are both surface area and direction of the axes of the confidence interval. This simulation shows very clearly that optimizing the experiments can result in a very significant increase in the accuracy of the

Table 1. Reactivity ratios as calculated by means of NLLS from equally distributed monomer feed composition (set 1) and optimized monomer feed composition (set 2)

	Set 1	Set 2	True values
r_{11}	0.069	0.107	0.100
r_{21}	0.455	0.276	0.300
r_{12}	0.278	0.188	0.200
r_{22}	0.320	0.414	0.400

Fig. 1. 95% Joint confidence intervals of the reactivity ratios from the simulated copolymerizations, r_{21} vs r_{11} .

obtained reactivity ratios. Therefore this method is used for the determination of apparent reactivity ratios for the copolymerization of styrene and maleic anhydride in various solvents.

EXPERIMENTAL

Materials

Styrene was dried over MgSO_4 , distilled at reduced pressure under N_2 at $35-40^\circ$ to remove the inhibitor and subsequently stored at -10° under N_2 . Styrene was always used within 24 hr after distillation.

Maleic anhydride was purified by vacuum sublimation at 50° and stored under N_2 . The initiator, α, α' -azobis(isobutyronitrile) (AIBN) was recrystallized from methanol, dried in a vacuum oven and kept refrigerated until required.

The solvents employed for polymerization were:

- toluene (Merck), purity >99.5%
- butanone (Riedel-de Haen), purity 99%
- $\text{N,N}'$ -dimethylformamide (Merck), purity >99.8%.

The solvents were dried over molecular sieves and were used without further purification.

Fig. 2. 95% Joint confidence intervals of the reactivity ratios from the simulated copolymerizations, r_{22} vs r_{12} .

All other chemicals were high purity grades and were used without further purification.

Polymerization

The required amounts of monomers and initiator were accurately weighed into 250 ml volumetric flasks. After the addition of solvent to obtain a homogeneous solution, the volumetric flasks were filled with the solvent and homogenized in the usual way.

The monomer and initiator concentrations are 2 and 2×10^{-3} M, respectively. The mixtures were transferred to 350 ml reaction vessels and deaerated (three freeze-thaw cycles). The copolymerizations were carried out at $60.0 \pm 0.1^\circ$ in a shaking thermostat. All polymerizations were carried to conversions <5% by weight, in order to minimize composition drift.

The polymers were isolated by addition of the reaction mixture to a 10-fold excess of 2-propanol. The conversion was determined gravimetrically. The copolymers were purified by reprecipitation from butanone solution into 2-propanol. The purified polymers were dried in vacuo at 60° for 24 hr.

Characterization

DEPT ^{13}C -NMR spectra were recorded on a Varian Unity 300 spectrometer at ambient temperature. Solutions were approx. 10% (w/v) in acetone d_6 for samples with high MANh content or in CDCl_3 for samples with lower MANh content. The compositions of the copolymers were determined (i) from the triad fractions determined by DEPT ^{13}C -NMR, (ii) using i.r. spectroscopy, from the ratio between the relative extinctions $E_{1855\text{ cm}^{-1}}/E_{1490\text{ cm}^{-1}}$, and (iii) by non-aqueous titration. MANh contents reported in this paper are arithmetic averages of these three determinations.

The DEPT ^{13}C -NMR technique to determine styrene centred triad distributions has been described earlier [12].

Experimental design

From previous studies, it was clear that MANh does not homopolymerize under conditions as employed here. This means that the copolymerization between styrene and MANh can be described by a simplified penultimate unit model, as indicated earlier [3]. Based on the mathematical descriptions of copolymer composition and triad distribution vs monomer feed composition, experimental design was carried out as outlined above.

As estimates for the reactivity ratios, values were chosen from the literature for SMA copolymerization in bulk at 60° ($r_{\text{SS}} = 0.0177$; $r_{\text{MS}} = 0.0288$) [13]. In Table 2, the calculated monomer feed compositions for optimal experiments are given for each of the calculations.

To obtain experimental evidence of the influence of the experimental design method, experimental series were built up as follows.

In toluene, only the values obtained from F_s -based calculations were used. Furthermore, these values were not used accurately, i.e. four experiments were carried out at $f_s = 0.938$ and four experiments at $f_s = 0.990$. Only two triad distributions have been determined.

In butanone, again only the values obtained from F_s -based calculations were used. However, in this case the

Table 2. Monomer feed compositions based on experimental design procedure using $r_{\text{SS}} = 0.0177$ and $r_{\text{MS}} = 0.0288$

Calculation based on:	f_s^1	f_s^2
F_s	0.958	0.995
F_{SSS}	0.972	0.995
$F_{\text{SSM}} + \text{MSS}$	0.927	0.994
F_{MSM}	0.904	0.982

Table 3. Results of SMA copolymerizations in toluene at 60°

f_s (mol.)	Conv. (wt %)	F_M (wt)	F_{SSS}	$F_{SSM-MSS}$	F_{MSM}
0.938	0.693	0.364			
0.936	0.418	0.364			
0.940	0.960	0.353	0.10	0.50	0.40
0.941	0.950	0.361			
0.990	1.250	0.201			
0.991	1.560	0.188	0.49	0.45	0.06
0.990	1.230	0.198			
0.990	1.510	0.201			

Table 4. Results of SMA copolymerizations in butanone at 60°

f_s (mol.)	Conv. (wt %)	F_M (wt)	F_{SSS}	$F_{SSM-MSS}$	F_{MSM}
0.939	1.169	0.354	0.10	0.58	0.32
0.931	2.110	0.356	0.10	0.57	0.33
0.958	1.826	0.322	0.19	0.60	0.21
0.960	1.170	0.321	0.12	0.61	0.27
0.960	2.023	0.316	0.24	0.57	0.19
0.960	0.142	0.313			
0.996	0.450	0.132	0.72	0.24	0.04
0.995	1.020	0.126	0.65	0.31	0.04
0.995	1.390	0.116	0.73	0.24	0.03

Table 5. Results of SMA copolymerizations in N,N'-dimethylformamide at 60°

f_s (mol.)	Conv. (wt %)	F_M (wt)	F_{SSS}	$F_{SSM-MSS}$	F_{MSM}
0.995	0.728	0.170	0.62	0.34	0.05
0.995*	0.259	0.179	0.55	0.41	0.05
0.958	3.409	0.334	0.12	0.58	0.30
0.958*	2.801	0.333	0.11	0.59	0.30
0.958	3.363	0.335	0.12	0.59	0.29
0.982	2.275	0.270	0.30	0.56	0.14
0.982*	2.077	0.312	0.30	0.57	0.14
0.982	1.519	0.276	0.28	0.58	0.14
0.928*	3.465	0.378	0.05	0.50	0.46
0.927	3.877	0.378	0.07	0.49	0.44
0.927*	4.224	0.378	0.06	0.50	0.44
0.994	0.968	0.182	0.58	0.37	0.05
0.994*	1.241	0.175	0.58	0.38	0.04
0.904	2.170	0.379	0.03	0.42	0.55
0.904*	3.170	0.390	0.04	0.44	0.52
0.904	2.831	0.369	0.03	0.43	0.54
0.972	1.690	0.313	0.18	0.60	0.22
0.972*	2.111	0.312	0.17	0.61	0.22
0.972	2.311	0.307	0.18	0.60	0.22

values were used as exactly as possible. All triad distributions were determined as input for the parameter estimation.

In DMF, all values for monomer feed composition were used. In this case, all triad distributions were also determined.

RESULTS

In Tables 3–5 the experimental results are given for the copolymerizations in toluene, butanone and DMF. From these data, apparent reactivity ratios are determined using a non-linear least squares procedure [10]. The data are interpreted using the penultimate unit model, where $r_{MM} = r_{SM} = 0$. The apparent reactivity ratios are given in Table 6.

To determine whether the observed differences in apparent reactivity ratios are significant, joint confidence intervals were calculated using the method of Hautus *et al.* [11]. These confidence intervals are graphically shown in Fig. 3.

Table 6. Apparent reactivity ratios as obtained from the data in Tables 2–4

Solvent	r_{SS}	r_{MS}	r_{SS}/r_{MS}
Toluene	0.0234	0.0442	0.53
Butanone	0.0242	0.0628	0.39
DMF	0.0176	0.0455	0.39
DMF*	0.0189	0.0446	0.42

*Reactivity ratios were determined from the eight experiments marked with an asterisk in Table 5.

It is clear that the 95% joint confidence intervals do not overlap. Therefore, it is concluded that the apparent reactivity ratios are significantly influenced by the solvent.

There appears to be a remarkable difference among the surface areas of the confidence interval of the three solvents. In the case of DMFs the number of experiments was significantly larger than for the other two solvents. The effect of the number of experiments was investigated separately by using only eight of the experiments. The confidence interval based on this calculation are indicated with an asterisk in Fig. 3 and Table 5 respectively. In this case, the effect of the number of experiments on the surface area of the confidence interval is not significant. Especially remarkable is the relatively large surface area of the confidence interval for MEK. Inspection of the numerical values of the modulus of the determinant calculated from the determined reactivity ratios for the different solvents and the monomer feed compositions as used in the experiments reveals the cause of the difference in surface area. The modulus of the determinant for MEK has a structurally lower value than in the case of toluene and DMF. The numerical value of the determinant appears to be related to the values of the reactivity ratios involved. The highest obtainable accuracy is therefore influenced by the values of the reactivity ratios.

In an earlier study it was found that the copolymerization of styrene and MANh could be interpreted using the bootstrap effect [3]. To confirm this, the triad distribution is plotted vs copolymer composition.

Fig. 3. 95% Joint confidence intervals of the reactivity ratios of SMA copolymerizations in various solvents. The confidence interval of DMF indicated with an asterisk is based on the eight experiments indicated similarly in Table 5.

Fig. 4. Styrene-centred triads vs the fraction styrene in the copolymer for SMA copolymerization in various solvents: butanone (●), DMF (○) and toluene (△). Drawn curves are calculated using $r_{SS}/r_{MS} = 0.43$.

Although there is some scatter, data from the different solvents appear to be described by one set of curves. The plotted curves in Fig. 4 were calculated using the arithmetic average of the r_{SS}/r_{MS} ratio over the three solvents ($\langle r_{SS}/r_{MS} \rangle = 0.43$).

There appears to be a minor systematic deviation of the ^{13}C -NMR measurements from the theoretically predicted values. There are two possible causes for this deviation:

- (1) composition drift during copolymerization
- (2) systematic error from the integration of the ^{13}C -NMR spectra.

The possibility of composition drift was evaluated by numerical inspection. Simulation of composition drift and subsequent averaging the copolymer composition and sequence distribution did not result in a satisfactory explanation of the observed deviation.

It is therefore assumed that the deviation is caused by a small systematic error in the integration of the ^{13}C -NMR spectra. The results do not suggest inapplicability of the penultimate unit model for the styrene/MAnh copolymerization. Firstly because the deviation is only small and secondly because previously recorded NMR spectra exhibited no anomalies [3].

Qualitatively, the bootstrap effect is characterized by independence of the monomer sequence distribution vs copolymer composition upon the solvent employed. From Fig. 4 it is clear that this independence is present.

Quantitatively, the results are difficult to interpret, either with the method using a composition independent distribution coefficient [3], or with a composition dependent distribution coefficient [4]. The most probable reason for this difficulty concerning quantification is the fact that MAnh does not homopolymerize. This results in two reactivity ratios being zero. Bearing in mind that the difference in polarity between styrene and MAnh is large, one would assume that a composition dependent distribution is needed for the description of the solvent effect

on this copolymerization. The practical problem arising from the absence of MAnh homopolymerization is that the coefficients for the distribution coefficient cannot be determined with acceptable precision.

CONCLUSIONS

From the simulated example, it is clear that the accuracy of apparent reactivity ratios depends largely on the comonomer feed ratio used in the experiments. The method proposed by Tidwell and Mortimer for the Mayo-Lewis model also applies to the penultimate unit model. The latter is taken as an example to show the general applicability of this technique for the determination of apparent reactivity ratios. The use of computers for numerical differentiation and maximization of the modulus of the determinant makes it possible to use more complex models in the experimental design method.

The experimental results on the styrene with maleic anhydride copolymerization show that there is a significant solvent effect on the apparent reactivity ratios.

The present results indicate that the copolymerization of styrene with maleic anhydride copolymerization qualitatively shows the bootstrap effect. Quantitative interpretation of the results in terms of the bootstrap effect is hampered most probably by the absence of maleic anhydride homopolymerization.

From these results, it is concluded that a rigorous test of the proposed methods for quantification of the bootstrap effect should be based on a carefully selected comonomer pair. The monomers must possess a reasonably large difference in polarity whereas the copolymer should preferably remain dissolved in the monomer solution at the low conversion employed. Furthermore, both monomers should be able to homopolymerize under the experimental conditions. Comonomer pairs worth studying in this respect include styrene/acrylic acid and styrene/acrylamide.

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