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Copolymerization of Styrene and Methyl Methacrylate in Ternary Oil-in-Water Microemulsions: Comments on a Paper by Gan *et al.*

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Introduction. It is widely accepted that the ratio of incorporation of two monomers in a copolymer is determined by the reactivity ratios and by the relative ratio of the monomers at the site of polymerization. In heterogeneous radical copolymerizations, *e.g.* emulsion polymerization, it is clear that considerable differences may exist between the ratio of the comonomers in the aqueous and organic phases.[1] Also for polymerizations that are considered homogeneous, considerable evidence has been reported for the occurrence of monomer partitioning.[2] One of the major effects of monomer partitioning is the significant influence of experimental conditions on experimentally determined reactivity ratios.[3]

In a recent publication by Gan *et al.*, a study was reported on the monomer reactivity ratios in ternary oil-in-water microemulsions.[4] The copolymerization of styrene (STY) with methyl methacrylate (MMA) is used as the model system in the specific study by Gan. Some of the interpretations in the paper by Gan are based on erroneous assumptions and may therefore be misleading.

In this communication, we want to indicate the points of concern with respect to these misinterpretations. There are two issues that will be discussed separately: (1) determination of reactivity ratios; (2) microstructure of copolymers.

Determination of Reactivity Ratios. In the past there has been quite some discussion on the best method to determine reactivity ratios. Approximately three decades ago, it was found that the best method to do this is by using optimally designed experiments in conjunction with nonlinear least squares parameter estimation.[5] This method provides the most accurate estimates of the reactivity ratios and also allows the construction of a confidence interval. Nevertheless, still numerous publications refer to the linearized methods for the determination of reactivity ratios, *e.g.* the Fineman−Ross and the Kelen−Tüdôs methods. These methods may give rise to erroneous parameter estimates.

Reinterpretation of the data by Gan was carried out using a nonlinear least squares error in variables (EVM) method.[6] Two different approaches were used: (1) Conversion is neglected; the instantaneous copolymer composition equation according to the terminal model (TM) is used. (2) Conversion is taken into account; by a numerical integration method, the average copolymer composition over the given conversion interval is calculated.

The point estimates of the reactivity ratios and their joint confidence interval are presented in Figure 1. The first approach leads to a fairly large confidence interval which contains the estimates of bulk copolymerization as given in Table 2 of Gan's paper (open circles) as well as the Kelen−Tüdôs estimate as calculated by Gan (×). This would lead to the conclusion that reactivity ratios in microemulsion are not significantly different from those determined in bulk copolymerization. The second approach takes conversion into account and leads to a smaller confidence interval. From a physical point of view, this approach is better; *i.e.* during the parameter estimation procedure, composition drift is simulated, and an average composition over the given conversion interval is obtained. The point estimate is given in Figure 1 by the open square. It is easily recognized that the confidence interval is much smaller (dotted line). Furthermore, the reactivity ratios from the bulk copolymerization are now slightly outside the confidence interval. As a next step, we carried out an EVM estimation on the complete data set as given in the paper by Gan. This means that copolymer composition and triad fractions as a function of comonomer feed composition were simultaneously used to carry out parameter estimation with respect to reactivity ratios in the terminal model. The procedure for numerical integration of the instantaneous copolymerization equation was also implemented in this parameter estimation procedure. The parameters obtained in this way have the highest degree of accuracy. The increased accuracy is recognized from the smaller confidence interval (dashed line). The point estimates of the different estimation procedures are summarized in Table 1. From Figure 1, it is easily recognized that a confidence interval around the bulk reactivity ratios would almost certainly overlap with the confidence interval of the microemulsion reactivity ratios. This observation translates into the conclusion that, on the basis of the present experimental results, no significant difference between the reactivity ratios in bulk and in microemulsion can be detected.

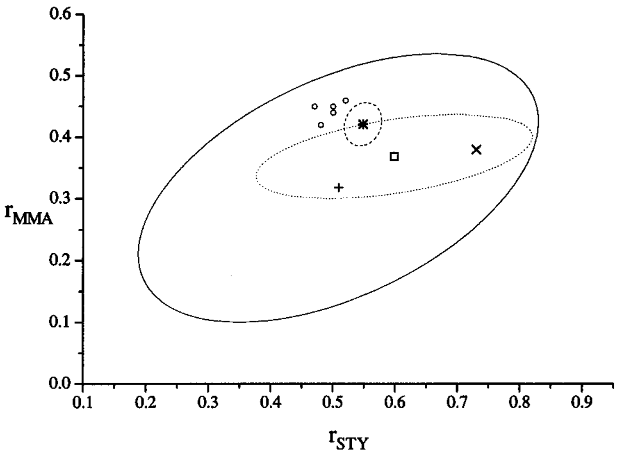

Figure 1. 95% joint confidence intervals of the various EVM estimations. (+, —) based on copolymer composition *vs* monomer feed composition, no compensation for composition drift; (□, ...) based on copolymer composition *vs* monomer feed composition, numerical integration of the Mayo−Lewis equation invoked; (*, - - -) based on copolymer composition and triad distribution *vs* monomer feed composition, numerical integration of the Mayo−Lewis equation invoked; (×) Gan's estimate for microemulsion; (○) Gan's summary of bulk copolymerization reactivity ratios.

Based on his estimated reactivity ratios, Gan calculated the relative comonomer fractions at the site of propagation. The approach Gan used was described a long time ago[7] and has recently also been used to describe the bootstrap effect.[8] The partition coefficient gives a numerical value for the ratio between the ratio of comonomers at the site of propagation on one hand

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Table 1. Point Estimates of Reactivity Ratios Based on Different EVM Procedures

	r_M	r_S
F_S *vs* f_S: no correction for composition drift	0.32	0.51
F_S *vs* f_S: Mayo–Lewis eq integrated	0.37	0.60
triads plus F_S *vs* f_S: Mayo–Lewis eq integrated	0.42	0.55
Gan's estimates for microemulsions[4]	0.38	0.73

and the ratio of comonomers in the feed on the other hand. Rewriting some of the equations for copolymer composition, as has been done before, leads to the expressions as given in the paper by Gan, which say that $r_S = r_S'K$ and $r_M = r_M'/K$, where K is the monomer partition coefficient. Based on reactivity ratios determined in microemulsion and determined in bulk, it is now possible to estimate K relative to bulk copolymerization; *i.e.* bulk copolymerization is used as a reference state. The difference between the two values thus calculated, one from r_S and one from r_M, may be caused by experimental inaccuracy but can also be caused by the difference in partition coefficient between the two homopolymers. This discussion is given in more detail in a previous paper on the bootstrap effect with the copolymerization of styrene and acrylonitrile.[9]

Gan uses an average value of the partition coefficient as a first approximation to determine the effect on the comonomer ratio at the site of propagation. This is a valid approach, but then the assumption that the fraction of styrene f_S' at the site of propagation equals that in the feed is invalid. This in turn would mean either that f_M' and f_M are also equal or that the sum of the fraction is no longer unity. Apparently, the latter is done by Gan, which inevitably leads to ratios of f_M'/f_M equal to $K^{-1} = 0.75$, which is illustrated in their Table 3. The calculation as performed by Gan is therefore no evidence that the MMA concentration at the site of propagation has a constant ratio to the value in the feed. The constancy of the ratio f_M'/f_M is a direct consequence of the definition of the partition coefficient and the assumption that $f_S' = f_S$.

Microstructure of Copolymers. A significant part of the discussion in the paper by Gan is on the microstructure of the copolymer, *i.e.* the monomer sequence distribution expressed as triad fraction versus copolymer composition. One of the major conclusions is that the experimentally determined microstructure is in good agreement with the calculated values based on the monomer reactivity ratios $r_S = 0.74$ and $r_M = 0.38$. It was shown in earlier studies that the monomer sequence distribution as a function of copolymer composition is *not* determined by the separate reactivity ratios, but by its product. If we take a closer look at the reactivity ratios as presented in Table 2 of the paper by Gan, it is easily recognized that the product of the reactivity ratios is not significantly influenced by bulk or microemulsion conditions. In bulk $r_Sr_M = 0.20 \pm 0.06$ and in microemulsion $r_Sr_M = 0.28 \pm 0.06$. In Figure 2, the experimental points from the paper by Gan are plotted together with calculated curves based on the bulk reactivity ratio product and based on the microemulsion reactivity ratio product (Gan's estimate and the best estimate according to the EVM method). From visual inspection, it is clear that all three sets of curves show comparable agreement with the experimental points.

Conclusions. The present re-evaluation of experimental data by Gan *et al.* leads to two main conclusions:

(1) The estimation of reactivity ratios should always be carried out by means of the error in variables method. The linearized methods may give rise to erroneous point estimates for the reactivity ratios, and, based on those, to ambiguous interpretation of experimental data.

(2) The monomer sequence distribution as a function of copolymer composition is determined by the product of the reactivity ratios (in the case of the terminal model). Monomer partitioning as discussed in this paper and in the original paper by Gan *et al.* does not influence the reactivity ratio product. This was one of the major conclusions resulting from quantitative considerations on the bootstrap effect, which is based on an identical approach.

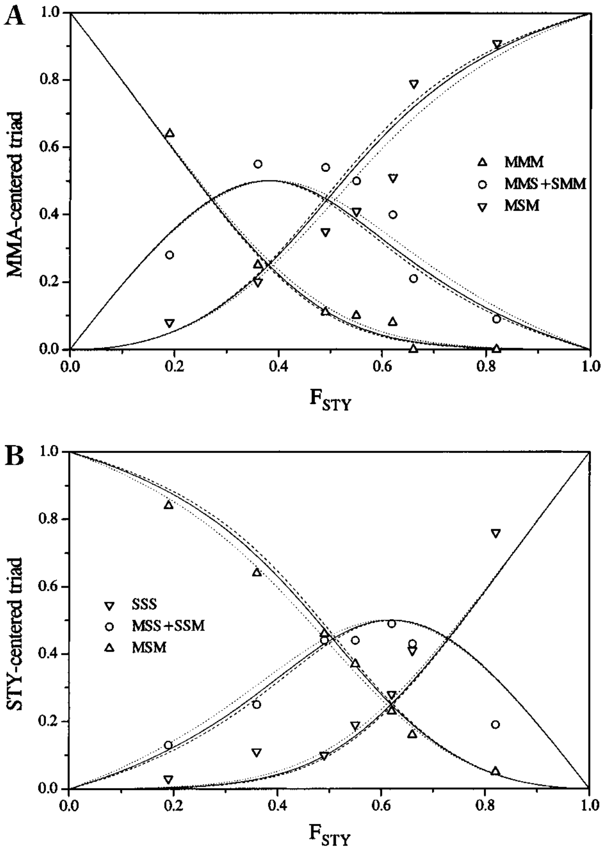

Figure 2. Triad fractions *vs* copolymer composition: Gan's experimental data[4] (legend in insert); drawn line, calculated curve based on EVM estimation ($r_M = 0.42$, $r_S = 0.55$); dashed line, calculated curve based on bulk reactivity ratios;[10] dotted line, calculated curves based on Gan's microemulsion reactivity ratios.[4] (A) MMA-centered triads; (B) styrene-centered triads.

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