Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Hagiopol, Cornel(2006) 'Solvent Effect in Binary Copolymerization', Journal of Macromolecular Science, Part A, 43: 3, 487 — 495

To link to this Article: DOI: 10.1080/10601320600575157

URL: http://dx.doi.org/10.1080/10601320600575157

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:487–495, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600575157

Solvent Effect in Binary Copolymerization

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Recently published experimental data concerning the solvent effect in binary copolymerization are re-analyzed. Newer, more accurate, reactivity ratios were calculated using a non-linear method (PROCOP), which involves all experimental data, conversion values included. The differences between the reactivity ratios provided by the recalculated values are discussed in terms of solvent effect. Based on the existing experimental data, the solvent effect was identified only for a few binary copolymerization systems.

Keywords copolymerization, reactivity ratios, estimation method, PROCOP computer program, solvent effect, conversion effect, analytical method

Introduction

The sequence distribution in a copolymer chain depends on the monomer feed composition, and on the monomer reactivity ratios. Many suggestions have been made to account for the differences in reactivity ratios noticed when copolymerizations are performed in different solvents: the supposed involvement of another kinetic model (1, 2), the solvent polarity, the effect of the radical-solvent complex and/or that of the monomer-solvent complex (3–6).

Even at very low conversions, the newly formed copolymer can change the local monomer concentrations, which become different from the average concentrations. The thermodynamic properties of the monomer mixture and of the solvent (if one monomer is a poor solvent for its resulting copolymer) lead to preferential sorption of monomers (bootstrap effect) (2, 4, 7–10). It is expected that some solvents will affect the copolymerization process. An attempt at providing a quantitative estimation of the solvent effects was made (10, 11).

Along with the chemical reactivity and the monomer concentrations, the solvent effect can be another factor that influences the copolymer composition. Given the importance of that issue, several reviews on the solvent effect on copolymerization have already been published (5, 6, 11–13).

Deviations from the expected copolymer composition and microstructure occur when the solvent effects on the propagation step or on the local comonomer concentrations are noted in free-radical copolymerizations. Unless those effects are considered, an incorrect calculation will be made of the "real" monomer reactivity in copolymerization. Many

Received July 2005; Accepted October 2005.
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authors have tried to record a solvent effect by looking at the reactivity ratio values. Any miscalculation in the reactivity ratio estimation may result in a wrong perception on the "real" solvent effect.

The "new" reactivity ratios, estimated for a particular solvent, are "apparent" reactivity ratios only. Researchers have tried to find a relationship between the apparent reactivity ratios and the 'real" reactivity ratios (14).

The accuracy of apparent reactivity ratio estimation depends largely on the comonomer feed ratios (experimental design) (15), the analytical method used, the conversion values and the estimation method (16). The kinetic model can also influence the reactivity ratio values recorded with different solvents (1, 17).

The present article focuses on the accuracy of the reactivity ratio estimation, and the impact of the lack of accuracy thereof on the final conclusions regarding the solvent effect in copolymerization.

Experimental

In order to find out which solvent has a significant effect on a copolymerization system, several examples of previously published experimental data will be presented in this article. The experimental data (feed ratios, copolymer composition and conversion values) are entirely taken from the original articles. The influence of the conversion values, the analytical method and the estimation methods on the reactivity ratios will be studied, in order to separate their effects from that of the "real" solvent effect in free radical copolymerization.

In order to obtain the best estimation for the reactivity ratios, a computer program (PROCOP) (18) has been used. The computer program runs an optimization (19) based on Simplex algorithm (Nelder and Mead) applied to the Mayo-Lewis equation in its integral form (20). That type of optimization has been taken over by several other scientists (17, 21, 22).

Results and Discussions

Many articles concerning the solvent effect in binary copolymerization were reviewed and a selection was performed. Articles with no explicit experimental data (23–26) or which contained few experimental points only (27) were not taken into consideration.

A "warning" system must operate for situations when a copolymerization reaction does not follow the well-known pattern of behavior. If a straight line does not fit the experimental points when a linear estimation method for reactivity ratios (KT or FR) is used, then the data interpretation is questionable (28).

The validity and importance of the Q-e scheme was revealed over the years (29). When a conflict with the Q-e scheme is noticed ($r_1 > 1.0$ and $r_2 > 1.0$ and/or $r_1r_2 > 1.0$, see acrylamide–MMA copolymerization (30) $r_{MMA} = 1.99$ and $r_{Aam} = 1.84$, solvent dioxane) attention must also be paid (and that is another warning sign) to a small detail hidden behind the experimental data: the solvent effect. According to the Q and e values published for those two comonomers (31) ($Q = 0.78$ and $e = 0.40$ for MMA and $Q = 0.23$ and $e = 0.54$ for acrylamide) the reactivity ratios estimated by using the Q-e scheme are very close to those calculated if a good solvent (DMSO) was used: $r_1 = 3.57$ and $r_2 = 0.27$.

Information about the reactivity ratio values should always be associated with the 95% confidence domain (the "real" reactivity ratios are located anywhere within the confidence domain). In order to separate a solvent effect based on the reactivity ratio modifications, we need to be able to clearly distinguish between the confidence domains.

How Easy is it to Identify the Solvent Effect?

The solvent effect is present when a difference in reactivity ratio values has been noticed. The question is: how large that difference should be in order to qualify as a "solvent effect". If the 95% confidence domain is taken as an associated characteristic of a particular set of experimental data, then any reactivity ratio pair located outside the confidence domain will be a proof for differentiation. However, in order to qualify that differentiation we have to make sure that the difference in reactivity ratios is due to the "solvent effect" and not to other collateral facts: analytical method, estimation method, and/or the quality of the experimental program.

The analytical method used accounts for many errors in the estimation of reactivity ratios. Figure 1 shows the 95% confidence domains for the copolymerization of MMA-St in several solvents (32). For each copolymer, two different analytical methods were used: the NMR and the carbon content analysis.

The option for one analytical method or another brings about modifications of the r_{ij} values that can be misattributed to the solvent effect. However, it is worthwhile concluding that in all cases illustrated by Figure 1, the NMR method provides smaller, i.e., more reliable, confidence domains.

Figure 1 clearly shows that in all cases under study, the use of different analytical methods results in getting different values for the reactivity ratios. Discrepancies may be so obvious that the analytically determined r_{ij} values can be identified outside the confidence domain of another analytic method (see solvent: benzonitrile).

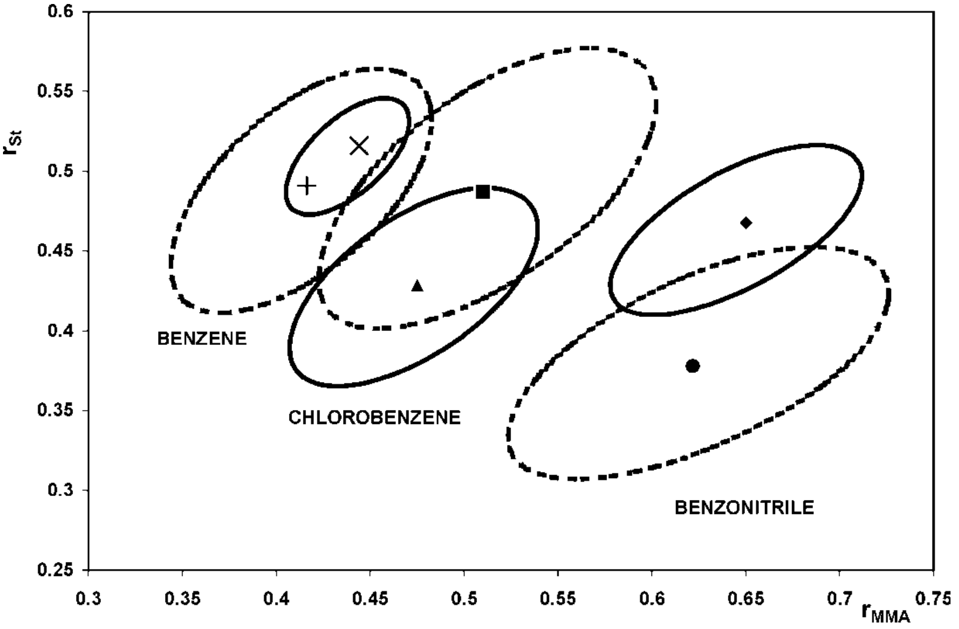

Figure 1. The approximate 95% confidence regions for the reactivity ratios of methyl methacrylate (M_1)–styrene copolymerization. The copolymer composition was measured by elemental analysis (doted curves) and by NMR.

The solvent effect in copolymerization is a wide topic, and results obtained in different labs should be collected in order to get a more complete picture of the issue. That is going to be a difficult task: the analytical method, the experimental program (comonomer ratio), the conversion values, the temperature, can trigger differences, which are not related to the solvent effect itself. The same styrene–methyl methacrylate copolymerization system as that presented in Figure 1 (at 60°C, in benzonitrile, and using the same analytical method: carbon analysis), was studied by both T.Ito and T.Otsu (33) and San Roman et al. (32). Surprisingly, the results are so largely different that the confidence domains do not even overlap (Figure 2).

The copolymerization reaction conversion is another factor, which should be taken into account (Figure 3) in reactivity ratio estimation, especially when $r_i \gg r_j$. In ethyl methacrylate (M1)–N-vinyl carbazole copolymerization in benzene (34) an important difference was recorded when the reaction was performed up to high conversions. At higher conversions (24.4–31.2%), the experimental errors are much more serious in terms of copolymer composition (see the confidence domain area). The reactivity ratios estimated for the high conversion experimental points are located outside the confidence domain for low conversion experimental data (1.6–9.9%). The conversion values should be kept at a very low level and should always be taken into account in the estimation method.

The estimation method can have an important impact on reactivity ratio values (16, 18), and conversion values may make things even more difficult. Figure 4 shows the confidence domains for the reactivity ratios estimated for N-vinyl carbazole–styrene copolymerization ($r_2 \gg r_1$) (35) using the Procop program which can use the copolymerization equation in its integral form. Regardless of the solvent type (DMF and benzene), the estimation methods, which use the differential equation (FR, KT and RREVM), are outside the confidence domain. In other words, when a gap in reactivity ratios is noticed, we have to make sure that the right estimation method was used.

When appropriate estimation and analytical methods are used, and when the conversion values are taken into account, the experimental data may or may not allow for the identification of a solvent effect.

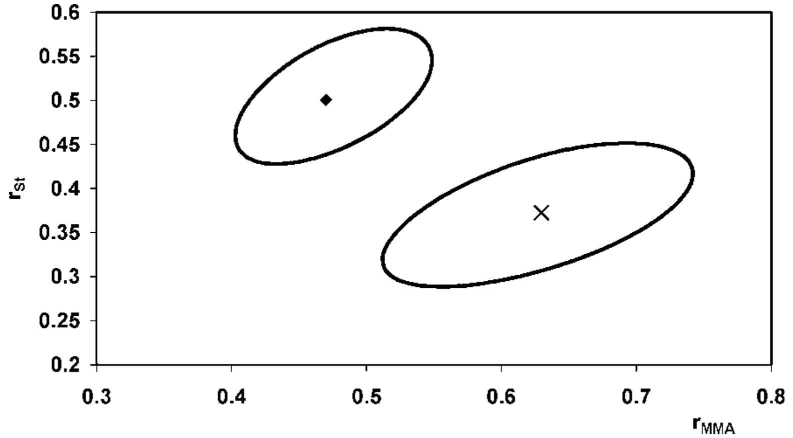

Figure 2. The approximate 95% confidence regions for the reactivity ratios of methyl methacrylate (M_1)–styrene copolymerization benzonitrile as solvent. The copolymer composition was determined by carbon analysis by San Roman et al. (32) (X) and Ito et al. (33) (◆).

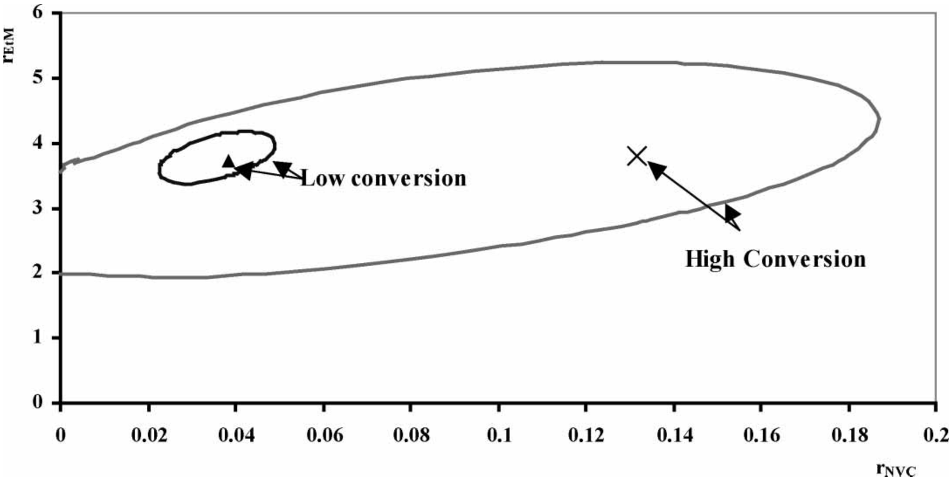

Figure 3. The approximate 95% confidence regions for the reactivity ratios for N-vinyl carbazole (M1)–ethyl methacrylate copolymerization in benzene.

Experimental Data Which Prevents the Identification of a Solvent Effect

The butyl methacrylate–MMA copolymerization was performed in bulk (36), ethanol (37), benzonitrile and benzene at different concentrations (38, 39). Figure 5 shows the confidence domains for those experiments and it can be seen that the solvent (benzonitrile or benzene) does not have a significant effect on the reactivity ratios: the reactivity ratios and the confidence domain are located within the confidence domain for bulk copolymerization. For lower experimental errors (for the copolymerization in benzonitrile and benzene) a solvent effect can be noticed. That differentiation is still under debate because both are included in the bulk 95% confidence region for the bulk copolymerization. A differentiation it is obvious when ethanol is used as a solvent (37). However, the entire picture is confusing (we can separate between the copolymerization

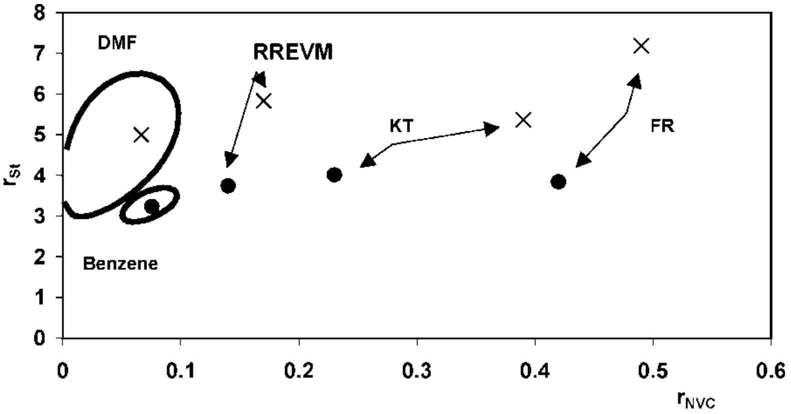

Figure 4. The approximate 95% confidence regions calculated by using the Procop method for the reactivity ratios for N-vinyl carbazole–styrene copolymerization in DMF (X) and benzene (●) as solvent; Reactivity ratios calculated by using RREVM, KT and FR methods are also presented.

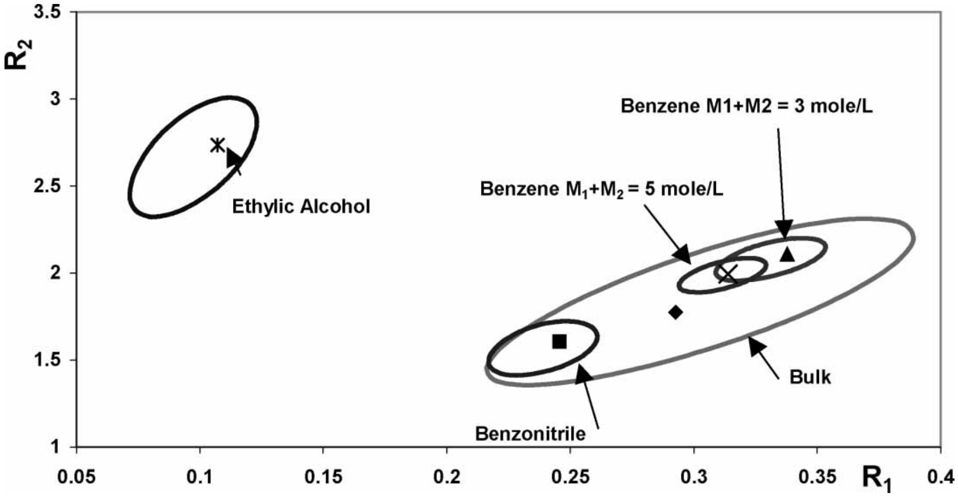

Figure 5. The approximate 95% confidence regions for the reactivity ratios with the butyl acrylate (M1)–methyl methacrylate copolymerization in bulk and in different solvents.

performed in different solvents, but we cannot separate solvent copolymerization from bulk copolymerization) and that can be due to the conflicting data provided by three different teams.

Matsuda et al. (3) published a very interesting study on Ethyl 4-Methyl-3-Oxo-4-Pentenoate–styrene copolymerization in different solvents. Unfortunately, the authors used the FR method and, for several systems, the reactivity ratios are located outside the confidence domain for the reactivity ratios calculated with a non-linear method. It is obvious that a re-evaluation of the experimental data is needed in order to reach an accurate conclusion.

For two very different solvents (in terms of polarity, DMF and benzene for instance) the experimental data may lead to a good separation of the confidence domains (Figure 6).

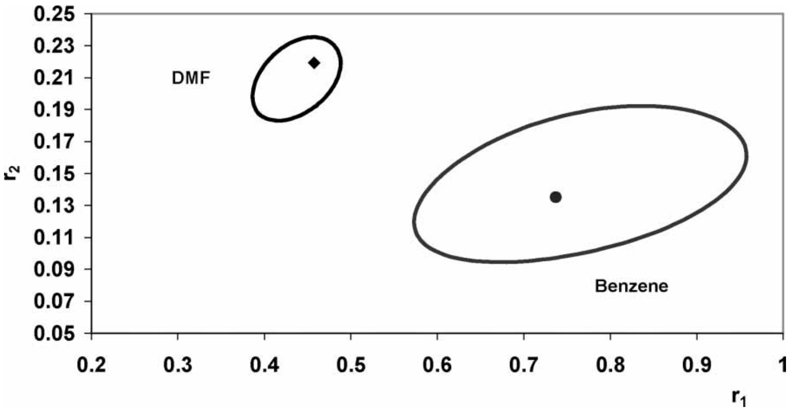

Figure 6. The approximate 95% confidence regions for the reactivity ratios for ethyl 4-Methyl-3-Oxo-4-Pentenoate(M1)–styrene copolymerization in DMF and benzene as solvent.

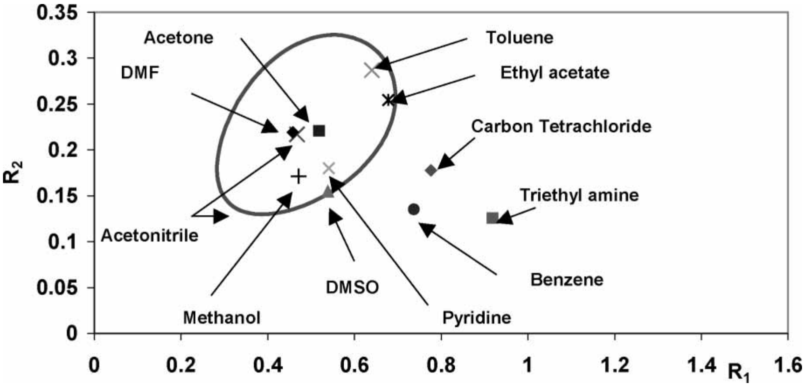

Figure 7. The approximate 95% confidence region for the reactivity ratios for ethyl 4-Methyl-3-Oxo-4-Pentenoate(M1)–styrene copolymerization in acetonitrile as solvent; Reactivity ratios calculated by the Procop method for different solvents are also presented.

In that case, it can be stated that the solvents have an important impact on copolymer composition. The authors tried to find a correlation between the solvent polarity and the monomer reactivity in copolymerization within an extended number of solvents: acetonitrile, acetone, benzene, carbon tetrachloride, DMF, DMSO, ethyl acetate, methanol, pyridine, toluene, triethyl amine. Figure 7 shows the confidence domain for a solvent with a medium polarity (acetonitrile) (40). Within that series of solvents the 95% confidence domain for acetonitrile reactivity ratios includes the reactivity ratios of many other solvents with very different polarities (40). Obviously, the solvent effect cannot be qualified for that copolymerization system and, based on those experimental data, a correlation of the reactivity ratios and solvent polarity is not supported by facts.

Experimental Data Able to Separate the Solvent Effect

The experimental data published (41, 42) for methacrylic acid-methyl methacrylate copolymerization in toluene, isopropyl alcohol, acetone and acetonitrile allow for the qualifying of the solvent effect (Figure 8). The difference in reactivity ratios for the

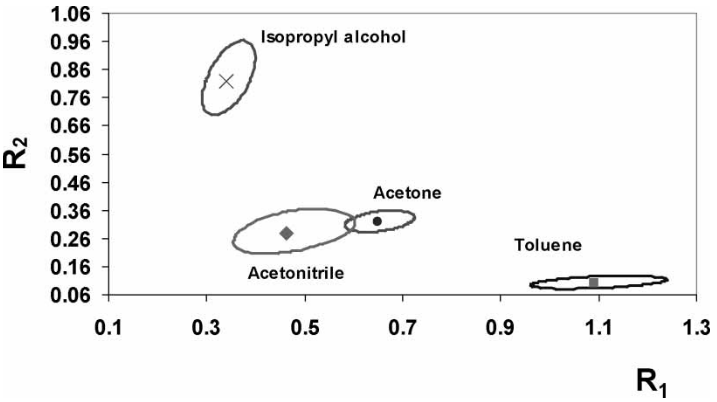

Figure 8. The approximate 95% confidence regions for the reactivity ratios for methacrylic acid (M_1) copolymerization with methyl methacrylate in different solvents.

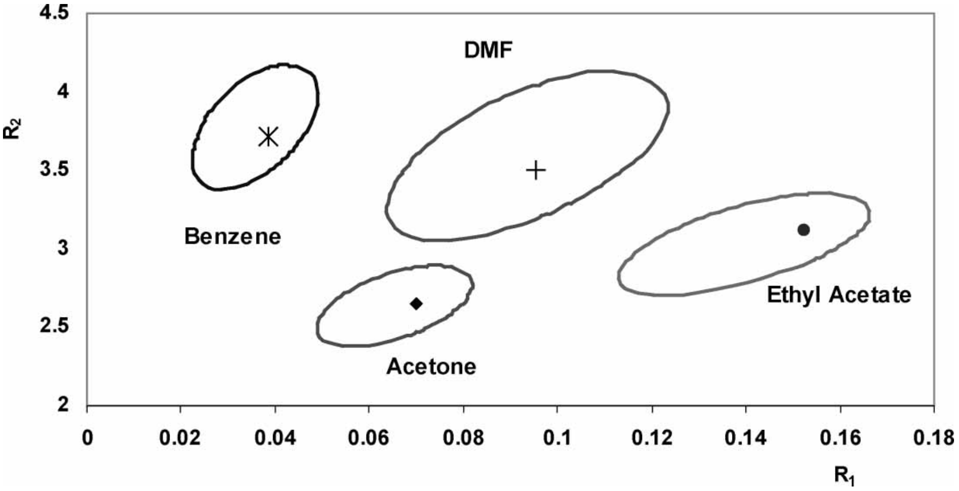

Figure 9. The approximate 95% confidence regions for the reactivity ratios for N-vinyl Carbazole (M_1) copolymerization with ethyl methacrylate in different solvents.

copolymerizations in acetonitrile and acetone is still questionable (the confidence domains are overlapping) but there is no doubt that there are important differentiations between isopropanol, acetonitrile (or acetone) and toluene.

Experimental data for the copolymerization of N-vinyl carbazole with ethyl methacrylate (34) allow for a distinction among the effect of benzene, ethyl acetate, acetone and N,N-dimethylformamide (Figure 9) on the reactivity ratios. It is clear that the 95% joint confidence domains do not overlap. Therefore, it is concluded that the apparent reactivity ratios are significantly influenced by the solvent. The nature of the solvent seems to be effective for both r_1 and r_2.

Conclusions

Based on composition data and reactivity ratio estimation, a solvent effect on copolymerization reactions can be identified. Statistically speaking, only few of the data sets provided by literature can allow for a reliable identification of the solvent effect in binary copolymerization.

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