LIVING CARBOCATIONIC COPOLYMERIZATIONS. II. REACTIVITY RATIOS AND MICROSTRUCTURE OF ISOBUTYLENE/p-METHYLSTYRENE COPOLYMERS

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A novel method was developed for the quantitative description of copolymerization behavior, specifically for the derivation of reactivity ratios and micro- and macro-compositions of monomer pairs with significantly different reactivities. The novelty of the method lies in the manner of generating instantaneous feed and copolymer composition data from experimentally readily obtainable cumulative copolymer compositions, although the latter drifts with progressing copolymerization. It is demonstrated that such copolymer systems can be described by two reactivity ratios, albeit the values are valid only over the narrow feed composition range within which they were determined. The great advantage of this method is that whereas the differential copolymer composition equation is strictly valid only at 0% conversion, the method produces corresponding instantaneous feed and copolymer compositions at any conversion. Assumptions or approximations are unnecessary to calculate reactivity ratios. Subsequently the procedure was applied to obtain reliable monomer reactivity ratios of isobutylene (IB)–p-methylstyrene (pMeSt) copolymers, r_{IB} and r_{pMeSt}, prepared by living carbocationic copolymerizations with [IB]/[pMeSt] feeds compositions of 90:10 and 97:3 mol/mol, i.e., with feed compositions of industrial importance. According to our procedure, $r_{IB} = 0.74 \pm 0.11$ and $r_{pMeSt} = 7.99 \pm 3.34$. These reactivity ratios were then used to calculate overall IB–pMeSt copolymer compositions over the *entire* comonomer conversion range and to compare calculated with experimental compositions. The good quantitative agreement between calculated and experimental compositions indicates that the description of both macro- and micro-compositions of IB–pMeSt copolymers obtained in the 90:10 and to 97:3 mol/mol feed composition range is satisfactory.

INTRODUCTION

Truly random copolymers are very difficult to produce if the structures (and therefore reactivities) of the participating comonomers are substantially different. In such cases the conventional copolymerization composition equation should not be used because the implied simplifications (i.e. copolymer composition is determined solely by the concentrations and reactivities of the two comonomers, etc.) do not hold (an excellent discussion of pitfalls to be avoided for the calculation of meaningful reactivity ratios appears in Ref. 1).

Recently, an attempt was made to describe the industrially important isobutylene (IB)–p-methylstyrene (pMeSt) copolymerization system by the conventional copolymer composition equation, and reactivity ratios which were similar (i.e. $r_{IB} = 0.99$ and $r_{pMeSt} = 1.43$) were published.[2,3] Subsequent work in which these r values were used to calculate IB and pMeSt sequence distributions for a series of IB–pMeSt copolymers, however, revealed significant discrepancies between the theoretically expected and experimentally determined (by ^{13}C NMR spectroscopy) data.[3] Our close examination of the spectroscopic data indicated that the reactivities of these monomers are indeed far different of those suggested by $r_{IB} = 0.99$ and $r_{pMeSt} = 1.43$. The large discrepancy between the calculated and experimental values may be due to the specific reaction conditions used (e.g. heterogeneous, non-living copolymerization).[2,3]

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The first objective of our work was to develop a novel method for the quantitative description of the copolymerization behavior of monomers having significantly different reactivities. We postulated that the composition of such systems could be described by the use of two reactivity ratios, albeit they will be valid only over a narrow feed composition range (say <10%), i.e. in the range within which they were determined. Necessarily, these reactivity ratios must be determined within a narrow feed composition range and their significance will rapidly diminish beyond this range.

We are aware that the determination of reliable reactivity ratios from only a few data points over a narrow feed composition range, particularly when this range is highly skewed in favor of one of the components, is fraught with uncertainty.[1] To avoid this pitfall, we derived equations to express quantitatively the relationship between instantaneous feed and copolymer compositions, and thus were able to calculate valid reactivity ratios by the two parameter copolymer composition equation (see Results and Discussion).

Our second objective was to apply this novel method to describe quantitatively the copolymerization (including reactivity ratios and micro- and macro-composition) of the technologically important IB–pMeSt monomer pair. We find that our method can be used in general for the characterization of the copolymerization behavior of monomers with significantly dissimilar reactivities. True, the quantitative description of copolymerizations by this method will be valid over only a narrow range of feed compositions; nontheless, many scenarios, particularly industrially important scenarios, can be envisioned in which quantitative information is needed over only a narrow feed composition range.[4]

EXPERIMENTAL

The experimental conditions and materials used were described in the preceding paper.[5]

RESULTS AND DISCUSSION

Reactivity ratio determination

Ideally, the differential copolymerization composition equation expresses the instantaneous copolymer composition as a function of an instantaneous feed composition. With increasing conversions, however, the composition of the instantaneous feed and, necessarily, the composition of the instantaneous copolymer will change, and this drift will be particularly strong with comonomer pairs having significantly different reactivities. Only when $r_1 = r_2 = 1$, or in azeotropic copolymerizations, will the copolymer and feed compositions remain constant with increasing conversions. In the IB–pMeSt system the monomer reactivities are markedly different (pMeSt is much

more reactive than IB) and the composition of the feed will change rapidly even at very low degrees of conversion. This drift in feed composition will result in a significant drift in copolymer composition and must be taken into account in order to calculate meaningful reactivity ratios.

One could overcome this problem of drifting feed and copolymer compositions and could obtain correct reactivity ratios by using either the integrated form of the copolymerization equation[6] or the Kelen–Tüdös (K–T) method[1] developed for high conversions.[7] The integrated method, however, is fraught with computational difficulties and the K–T method[7] provides meaningful reactivity ratios only if the two parameter copolymer composition equation is valid over the *entire* feed composition range. We reasoned that even if the copolymer composition does not hold over the entire feed composition range, it may still be applicable for monomer pairs exhibiting substantially different reactivities over a *narrow* feed range. We therefore proceeded to develop a new procedure to obtain precise composition information over a narrow feed composition range. The novelty of our method lies in the manner of generating instantaneous feed and copolymer composition data from experimentally readily obtainable cumulative copolymer compositions, although the latters drift with progressing copolymerization. These true differential feed and corresponding copolymer compositions can be used to calculate reliable monomer reactivity ratios by the K–T method[1] without any assumptions. These reactivity ratios, however, will be valid over only a very narrow feed composition range within which they were determined.

To test our procedure, we applied it to the industrially important IB–pMeSt copolymerization system. Thus, experiments were carried out with [IB]/[pMeSt] = 90 : 10 and 97 : 3 mol/mol feed compositions up to various conversions (cf. Ref. 5), and determined overall copolymer compositions by dual detector (RI and UV) gel permeation chromatography (GPC) using Fodor's algorithm.[8] Figures 1 and 2 show the data for the [IB]/[pMeSt] = 90 : 10 experiments: Evidently, at this feed composition the difference between weight and molar conversions is insignificant ($C_W \approx C_M$). Figure 1 shows cumulative (integral average) copolymer composition as a function of total monomer conversion. The cumulative and instantaneous copolymer compositions, f_c and f_i, and conversion C are interrelated by

$$\frac{\int_0^C f_i \, dC}{C} = f_c \quad (1)$$

To calculate r_{IB} and r_{pMeSt} by the differential copolymer composition equation, we need the instantaneous copolymer composition (f_i) and the instantaneous feed composition (F_i). We obtained f_i by computer fitting f_c
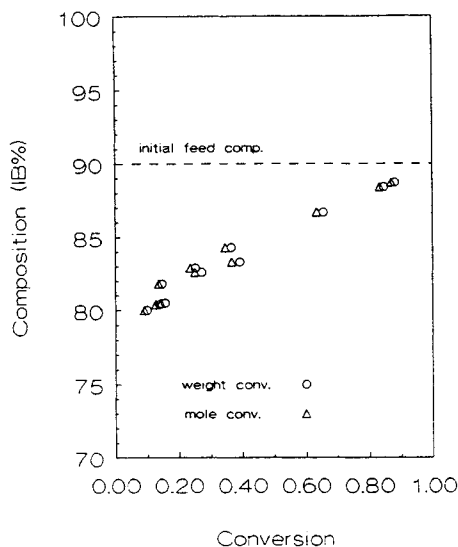
Figure 1. Cumulative IB content of IB–pMeSt copolymers as a function of conversion. Initial feed: [IB]/[pMeSt] = 90:10 mol/mol
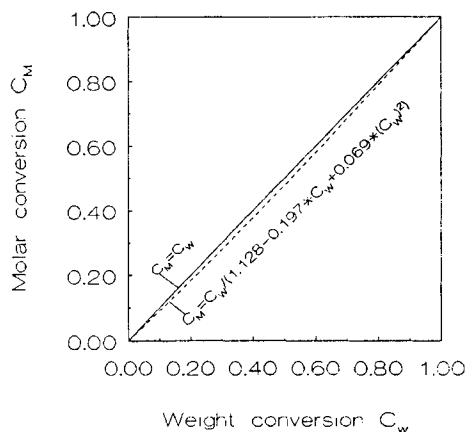

Figure 2. Molar conversion vs weight conversion in IB–pMeSt copolymerization. Initial feed: [IB]/[pMeSt] = 90:10 mol/mol

(in mol%) as a function of conversion by a polynomial function (see Figures 1 and 3):

$$f_c = 79 \cdot 8 + 11 \cdot 1 C - C^2 \qquad (2)$$

and expressed f_i from equation (1) as

$$f_i = \frac{\mathrm{d}}{\mathrm{d}C}(f_cC) = \frac{\mathrm{d}}{\mathrm{d}C}(79 \cdot 8 C + 11 \cdot 1 C^2 - C^3) \qquad (3)$$

$$f_i = 79 \cdot 8 + 22 \cdot 2 C - 3 C^2 \qquad (4)$$

F_i as a function of conversion can be derived from f_c and the material balance as follows. The total weight of the initial feed is the sum of the weights of the two monomers in the feed:

$$W_{\mathrm{total}} = W_{\mathrm{IB}} + W_{\mathrm{pMeSt}} \qquad (5)$$

and the weight of the copolymer:

$$W_{\mathrm{copolymer}} = W_{\mathrm{total}} C_{\mathrm{w}} \qquad (6)$$

where C_{W} is the weight conversion, hereafter simply C, because the molar and weight conversions are virtually indistinguishable ($C_{\mathrm{M}} \approx C_{\mathrm{W}}$, see Figure 2). Hence

$$W_{\mathrm{feed}} = W_{\mathrm{total}}(1 - C) \qquad (7)$$

and

$$W_{\mathrm{copolymer}} = W_{\mathrm{PIB}} + W_{\mathrm{PpMeSt}} \qquad (8)$$

where W_{PIB} and W_{PpMeSt} are the weights of the IB and pMeSt units in the copolymer.

At any moment during a copolymerization, the weights of IB and pMeSt in the feed are equal to $W_{\mathrm{IB}} - W_{\mathrm{PIB}}$ and $W_{\mathrm{total}}(1 - C) - (W_{\mathrm{IB}} - W_{\mathrm{PIB}})$, respectively. W_{PIB} is a function of f_c and C, and for the [IB]/[pMeSt] = 90:10 feed

$$W_{\mathrm{PIB}} = \frac{0 \cdot 01 f_c \dfrac{M_{\mathrm{IB}}}{M_{\mathrm{pMeSt}}} W_{\mathrm{total}} C}{1 - 0 \cdot 01 f_c \left(1 - \dfrac{M_{\mathrm{IB}}}{M_{\mathrm{pMeSt}}}\right)} \qquad (9)$$

where M_{IB} and M_{pMeSt} are the molecular weights of the monomers. Thus, from the definition of the mole fraction of IB in the feed,

$$F_i = \frac{100 \dfrac{(W_{\mathrm{IB}} - W_{\mathrm{PIB}})}{M_{\mathrm{IB}}}}{\dfrac{(W_{\mathrm{IB}} - W_{\mathrm{PIB}})}{M_{\mathrm{IB}}} + \dfrac{W_{\mathrm{total}}(1 - C) - (W_{\mathrm{IB}} - W_{\mathrm{PIB}})}{M_{\mathrm{pMeSt}}}} \qquad (10)$$

Figure 3 shows f_c, f_i and F_i vs C plots computed by this procedure. These F_i and f_i are true instantaneous values, and can be used without any assumptions to calculate r_{IB} and r_{pMeSt} by the differential copolymer composition equation.[9,10] Figure 3 provides all the needed corresponding F_i and f_i data pairs for the [IB]/[pMeSt] = 90:10 system. The instantaneous feed composition (F_i) changes from 90% IB to ca 100%, whereas the corresponding copolymer composition (f_i) increases from ca 80% to 100% with increasing conversion (at close to 100% conversion the calculation becomes unreliable owing to the large error). Figure 4 shows copolymer composition as a function of feed composition. These data were used to determine r_{IB} and r_{pMeSt} by the (K–T) method.[1]
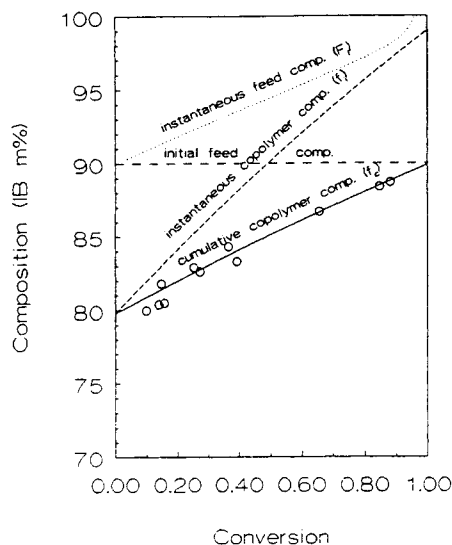
Figure 3. Cumulative copolymer composition experimental points and computer-fitted line), f_c, and computed instantaneous feed and copolymer compositions, F_i and f_i, as a function of conversion at $[IB]/[pMeSt] = 90:10$ initial feed composition

The K–T equation is a linearized version of the differential form of the copolymer composition equation:[9,10]

$$y = x \frac{1 + r_{pMeSt}x}{r_{IB} + x} \qquad (11)$$

where

$$y = \frac{dm_{pMeSt}}{dm_{IB}} \quad \text{and} \quad x = \frac{m_{pMeSt}}{m_{IB}} \qquad (12)$$

and dm_{pMeSt} and dm_{IB} are the instantaneous or differential composition ratios of copolymer and m_{pMeSt} and m_{IB} are those of the monomers. In the K–T equation,[1]

$$\eta = \left(r_{pMeSt} + \frac{r_{IB}}{\alpha}\right)\xi - \frac{r_{IB}}{\alpha} \qquad (13)$$

The variables are

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \qquad (14)$$

where

$$G = \frac{x(y-1)}{y} \quad \text{and} \quad F = \frac{x^2}{y} \qquad (15)$$

and α is a parameter that distributes symmetrically the experimental points between 0 and 1 along the ξ axis.
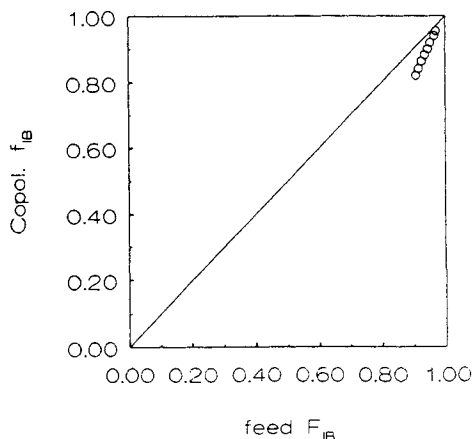

Figure 4. Instantaneous IB content in copolymer vs feed at $[IB]/[pMeSt] = 90:10$ initial feed composition

Figure 5(a) shows a three-dimensional K–T plot together with error contours [i.e. $\Delta = \pm 0.003$ absolute analytical error in copolymer composition determination ($\pm 0.3\%$) expressed in mole fraction]. The χ axis in Figure 5(a) shows the mole fraction of pMeSt in the feed before the K–T treatment, and helps to identify the corresponding instantaneous feed and copolymer composition data (see dotted drop-lines, and Figure 4 for feed and copolymer compositions before linearization). Since the K–T method gives linear plots only in terms of η vs ξ, Figure 5(b) shows such a plot and exhibits the linearized experimental points, the fitted straight line and the above error curves (dotted lines). The intercepts of the plot, based on equation (13), yield the reactivity ratios $r_{pMeSt} = 7.99 \pm 3.34$ and $r_{IB} = 0.74 \pm 0.11$ at $\alpha = 0.03$.

The great advantage of this method is that whereas the differential copolymer composition equation [(equation (11)] is strictly valid only at 0% conversion, this method produces corresponding instantaneous feed and copolymer compositions at any conversion, and assumptions or approximations are unnecessary to calculate reactivity ratios from equation (11) or (13).

Figure 6 shows experimental data together with computed instantaneous feed and copolymer composition curves obtained in copolymerizations with 97/3 $[IB]/[pMeSt] = 97:3$ feed at various temperatures (cf. Part I[5]). By applying our procedure (see above) we have generated the needed instantaneous feed and copolymer composition data, and thus calculated $r_{pMeSt} = 6.19 \pm 2.71$ and $r_{IB} = 0.69 \pm 0.05$ at $\alpha = 0.017$.

Figure 7 shows the K–T plot containing all the experimental data obtained in these investigations with both the $[IB]/[pMeSt] = 90:10$ and $97:3$ feeds (i.e. also those shown in Figure 3). The data show satisfactory linearity, which is an indication of
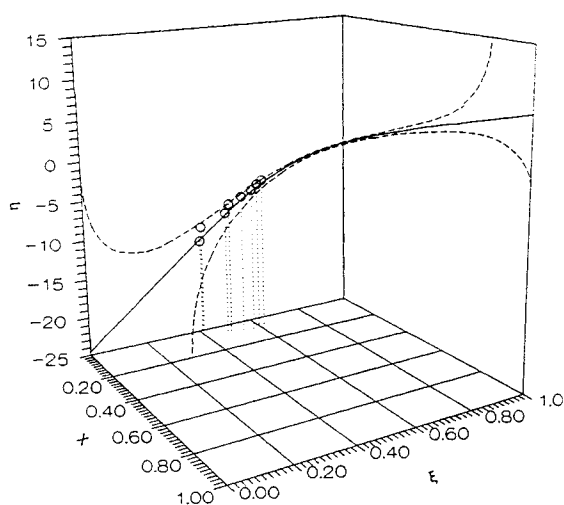
(a)
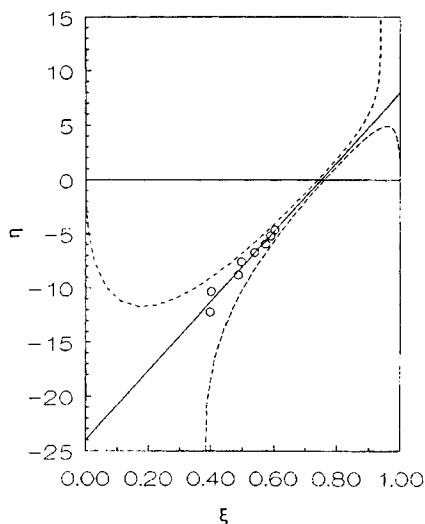
(b)

Figure 5 (a) Three-dimensional Kelen–Tüdős plot with error contours. See text for the meaning of the axes. (b) Kelen–Tüdős plot with error contours for [IB]/[pMeSt] = 90:10 initial feed composition. The error limits correspond to ±0·3% analytical error in copolymer composition determination
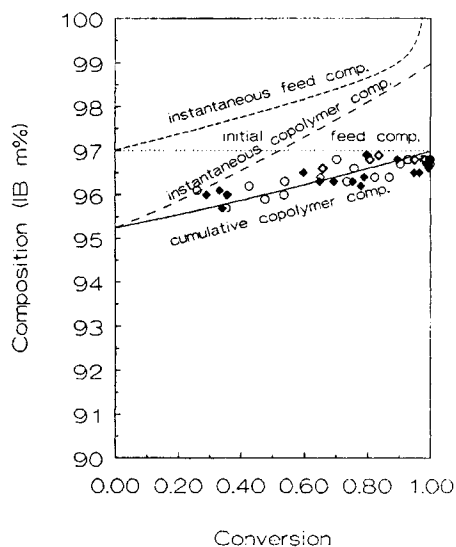

Figure 6. Experimental cumulative copolymer composition and computed instantaneous feed and copolymer compositions as a function of conversion at [IB]/[pMeSt] = 97:3 initial feed composition at (●) −40, (○) −52, (◆) −65 and (◇) −85 °C
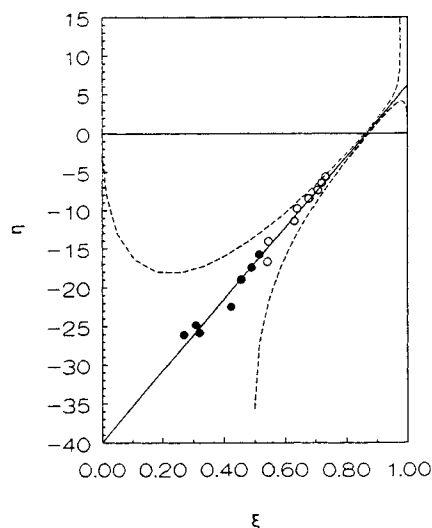

Figure 7. Kelen–Tüdős plot with error contours for [IB]/[pMeSt] = 90:10 (○) and 97:3 (●) initial feed compositions. The error limits correspond to ±0·3% analytical error in copolymer composition determination

reliable reactivity ratios. In further calculations we decided to use $r_{pMeSt} = 7·99 ± 3·34$ and $r_{IB} = 0·74 ± 0·11$, i.e. values obtained with the 90:10 feed, because these set of values, on account of the wider error limits, also embrace the values generated with the 97:3 feed.

Figure 8 shows copolymer compositions as a function of feed compositions. Our reactivity ratios are valid only over the limited composition range where data are available, and they certainly should not be used over the entire composition range.[11]
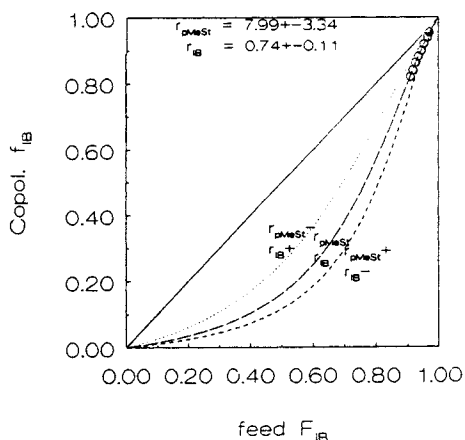
Figure 8. Experimental points and calculated copolymer composition curves together with error limits for [IB]/[pMeSt] = 90 : 10

Simulation of the IB–pMeSt copolymerization system

On the basis of reliable reactivity ratios (see the previous section), we were able to simulate the behavior of the IB–pMeSt copolymerization system (i.e. calculate the cumulative and instantaneous copolymer compositions as a function of conversion), and quantitatively to substantiate the correctness of our method by comparing the experimental data with computer fitted/calculated curves [cf. equations (1)–(10) and Figures 3 and 6).

First we calculated the molar conversion as a function of the instantaneous feed composition, using the closed integrated form of the Skeist equation:[6,12–14]

$$C = 1 - \left(\frac{F_{pMeSt}}{F_{pMeSt,0}}\right)^{\alpha}\left(\frac{F_{IB}}{F_{IB,0}}\right)^{\beta}\left(\frac{F_{pMeSt,0} - \delta}{F_{pMeSt} - \delta}\right)^{\gamma} \quad (16)$$

where C is molar conversion, $F_{pMeSt,0}$ and $F_{IB,0}$ are initial mole fractions of the respective monomers in the feed, F_{pMeSt} is the instantaneous mole fraction of pMeSt in the feed and

$$\alpha = \frac{r_{IB}}{1 - r_{IB}} \quad (17)$$

$$\beta = \frac{r_{pMeSt}}{1 - r_{pMeSt}} \quad (18)$$

$$\gamma = \frac{1 - r_{pMeSt}r_{IB}}{(1 - r_{pMeSt})(1 - r_{pMeSt})} \quad (19)$$

$$\delta = \frac{1 - r_{IB}}{2 - r_{pMeSt}r_{IB}} \quad (20)$$

Since we need the instantaneous feed composition (F_{pMeSt}) as a function of conversion (C), the inverse function of equation (16) was computer generated and used to calculate the instantaneous copolymer composition (f_{pMeSt}) as a function of conversion. For this calculation, the differential copolymer composition equation [equation (11)] was used, expressed in molar fraction for the total conversion range:

$$f_{pMeSt} = \frac{F^2_{pMeSt}(r_{pMeSt} - 1) + F_{pMeSt}}{r_{IB} + 2F_{pMeSt}(1 - r_{IB}) + F^2_{pMeSt}(r_{pMeSt} + r_{IB} - 2)} \quad (21)$$

The cumulative (average) copolymer composition function was computed from equations (1) and (21). The simulation was carried out for both [IB]/[pMeSt] = 90 : 10 and 97 : 3 initial feed compositions. The results are shown in Figures 9 and 10.

The points show simulated data calculated by using $r_{pMeSt} = 7.99$ and $r_{IB} = 0.74$ and equations (16) and (21), the solid lines show the computer fitted cumulative copolymer compositions based on experimental data and the broken lines were calculated by our procedure. The very good agreement between the simulated points and computed lines indicates that our procedure yields reliable reactivity ratios provided that they are sufficiently different to cause drifting of both feed and copolymer compositions even at extreme compositions and narrow composition ranges.

Microstructure studies

Accurate reactivity ratios are of great practical importance for predicting and controlling overall copolymer compositions and microarchitectures. Since in our system $r_{pMeSt} \gg r_{IB}$, the growing copolymers with pMeSt⁺ termini will tend to produce pMeSt sequences and, in addition, the continuously changing feed composition (continuous decrease in [pMeSt]) will give rise to macro- and micro-compositional heterogeneity.

The characterization of compositional heterogeneity and the determination of reactivity ratios from compositional distributions of copolymers by NMR spectroscopy are well known.[15,16] We calculated instantaneous and cumulative triad proportions as a function of conversion for the IB–pMeSt copolymerization system. For the calculation, we used $r_{pMeSt} = 7.99$ and $r_{IB} = 0.74$ and the instantaneous feed composition vs conversion function which characterizes the compositional shift in the feed during copolymerization.

The probability of forming a triad can be calculated by multiplying the probabilities of forming the corresponding consecutive diads. The probability of forming a pMeSt–pMeSt diad ($p_{pMeSt,pMeSt}$) is given by the ratio:

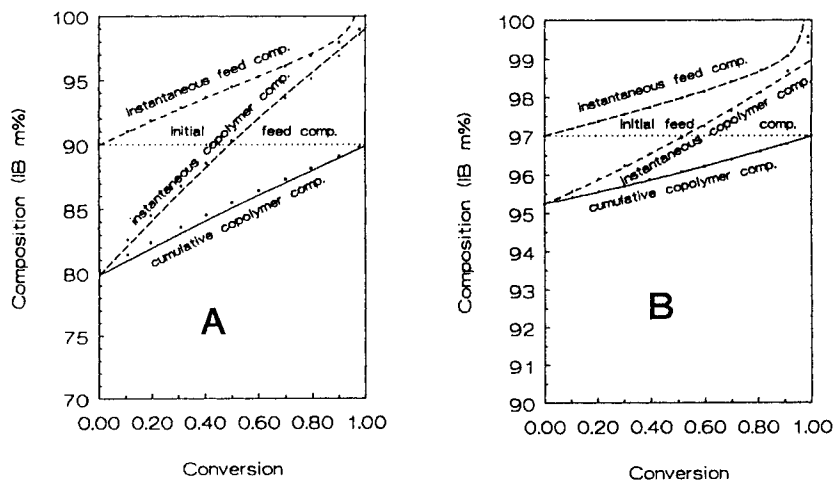$$p_{pMeSt,pMeSt} = \frac{R_{pMeSt,pMeSt}}{R_{pMeSt,pMeSt} + R_{pMeSt,IB}} \quad (22)$$

Figure 9. Cumulative and instantaneous copolymer composition and instantaneous feed composition as a function of conversion for [IB]/[pMeSt] =(A) 90:10 and (B) 97:3. Lines: fitted and calculated; points: simulated values (see text for details)

where $R_{pMeSt,pMeSt}$ is the rate of a growing $pMeSt^+$ cation adding pMeSt and $R_{pMeSt,IB}$ is that of a growing $pMeSt^+$ cation adding IB.[17].

By substituting the homo- $(R_{pMeSt,pMeSt})$ and cross-propagation $(R_{pMeSt,IB})$ rates with concentrations and reactivity ratios, and simplifying, one obtains the probabilities for the formation of the various diads:

$$P_{pMeSt,pMeSt} = \frac{r_{pMeSt}[pMeSt]}{r_{pMeSt}[pMeSt] + [IB]} \quad (23)$$

$$P_{pMeSt,IB} = \frac{[IB]}{r_{pMeSt}[pMeSt] + [IB]} \quad (24)$$

$$P_{IB,pMeSt} = \frac{[pMeSt]}{r_{IB}[IB] + [pMeSt]} \quad (25)$$

$$P_{IB,IB} = \frac{r_{IB}[IB]}{r_{IB}[IB] + [pMeSt]} \quad (26)$$

where [pMeSt] and [IB] are the conversion-dependent monomer concentrations in the feed.

We were interested in the relative probabilities of forming the four different triads with pMeSt, i.e. IB–pMeSt–IB abbreviated as BSB, IB–pMeSt–pMeSt (BSS), pMeSt–pMeSt–IB (SSB) and pMeSt–pMeSt–pMeSt (SSS). The probabilities of the formation of these triads can be expressed as follows:

$$P_{BSB} = \frac{p_{SB}p_{BB}}{p_{SB}p_{BB} + 2p_{SS}p_{SB} + p_{SS}^2} \quad (27)$$

(since ^{13}C NMR spectroscopy does not distinguish between BSS and SSB, each ...BSSB... unit will be represented by two BSS triads in the spectrum; therefore, we multiplied the probability of forming BSS

triads by 2):

$$P_{BSS+SSB} = \frac{2p_{SS}p_{SB}}{p_{SB}p_{BB} + 2p_{SS}p_{SB} + p_{SS}^2} \quad (28)$$

and

$$P_{SSS} = \frac{p_{SS}^2}{p_{SB}p_{BB} + 2p_{SS}p_{SB} + p_{SS}^2} \quad (29)$$

Similarly to compositions, triad proportions will also change as the feed composition shifts toward the less reactive monomer with increasing conversion. Hence instantaneous triad proportions can be calculated by substituting the instantaneous feed compositions [equation (10)] into the diad probabilities [equations (23)–(26)]. Figure 10 shows the results. With increasing
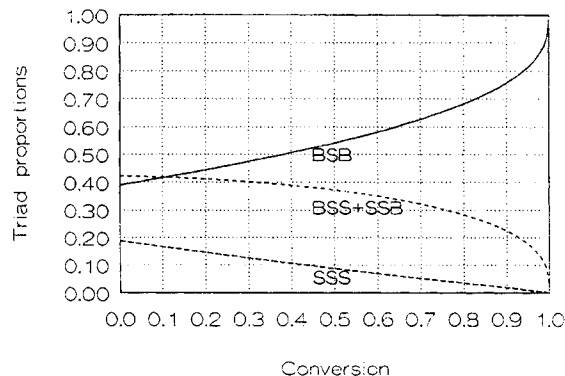

Figure 10. Instantaneous triad proportions as a function of conversion for the [IB]/[pMeSt] = 90:10 system

conversion (i.e. with decreasing [pMeSt] in the feed), the proportion of the BSB triads increases while those of BSS + SSB and SSS decrease.

The cumulative (average) triads P_{BSB}, P_{BSS} and P_{SSS} can be estimated as integral averages of the instantaneous triads:

$$P_{BSB} = \frac{\int_0^C p_{BSB}\, dC}{C} \qquad (30)$$

$$P_{BSS} = \frac{\int_0^C p_{BSS}\, dC}{C} \qquad (31)$$

and

$$P_{SSS} = \frac{\int_0^C p_{SSS}\, dC}{C} \qquad (32)$$

P_{BSB}, P_{BSS} and P_{SSS} were computer integrated from the corresponding instantaneous triads. Figure 11 shows the results for the [IB]/[pMeSt] = 90 : 10 system and Figure 12 shows the instantaneous (thin lines) and cumulative (thick lines) triad proportion functions for the [IB]/[pMeSt] = 97 : 3 system. Similarly to the cumulative and instantaneous copolymer compositions, the cumulative triad proportions vary less than the instantaneous triads with conversion (cf. Figures 3 and 6).

Cumulative triad proportions vs conversions can be related to NMR microstructure data, since the latter were obtained at finite conversions.[18] Figure 13 shows calculated cumulative triad proportions as a function of conversion for the [IB]/[pMeSt] = 97 : 3 system. The dotted lines show error limits caused by the errors in r_{pMeSt} and r_{IB}. The + sign indicates the case when $r_{pMeSt} + \Delta r_{pMeSt}$ and $r_{IB} - \Delta r_{IB}$ (that is, when the difference between the reactivity ratios is maximum), while
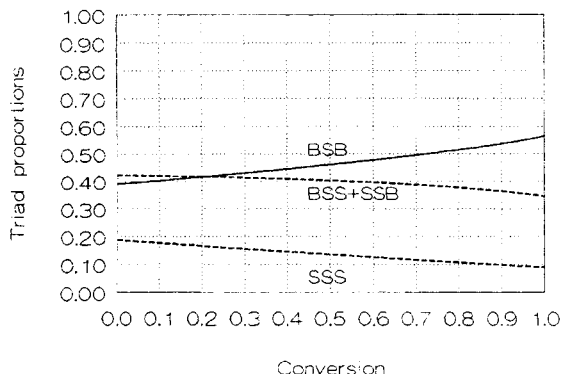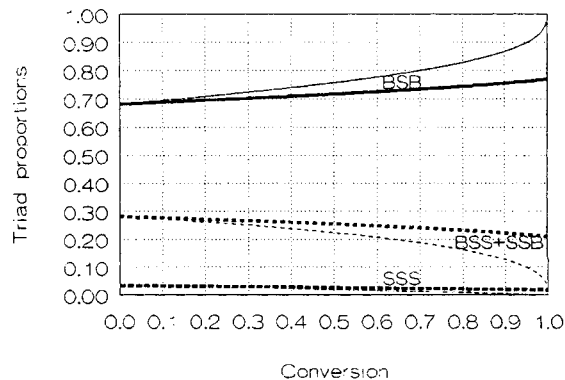

Figure 12. Instantaneous (thin lines) and cumulative (thick lines) triad proportions as a function of conversion for the [IB]/[pMeSt] = 97 : 3 system

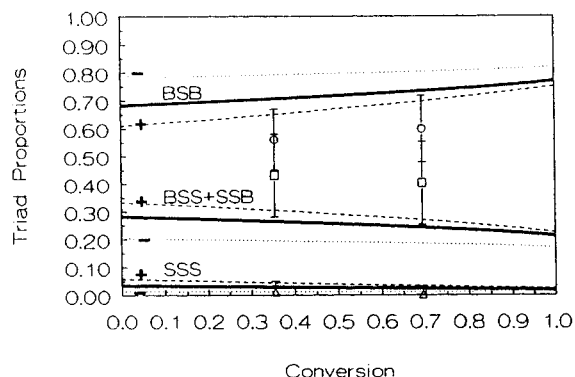Figure 13. Cumulative triad proportions (solid lines) with error limits (dotted lines) calculated from the reactivity ratios, and experimental data (O) BSB; (□) BSS; (△) SSS. Determined by ^{13}C NMR spectroscopy[18] for the [IB]/[pMeSt] = 97 : 3 system

the − sign indicates the case when $r_{pMeSt} - \Delta r_{pMeSt}$ and $r_{IB} + \Delta r_{IB}$ (that is when the difference between the reactivity ratios is minimum).

Figure 13 also shows the results of two sets of ^{13}C NMR (50.3 MHz) measurements on samples obtained at two conversions. Details of these NMR investigations will be published elsewhere.[18] Since the experimental points are reasonably close to the calculated curves, the agreement between the calculated and measured triad proportions is regarded as quite satisfactory. Thus, within this narrow but technologically significant composition range ([pMeSt] ≤ 10 mol% in the initial feed), our copolymerization can be satisfactorily described by the terminal model (two-parameter copolymer composition equation), and the r_{pMeSt} and r_{IB} values determined by our method satisfactorily expresses the

Figure 11. Cumulative triad proportions as a function of conversion for the [IB]/[pMeSt] = 90 : 10 system

macro- and micro-composition of IB–pMeSt copolymers.

CONCLUSIONS

A new method has been developed and tested for the quantitative characterization of copolymerization of comonomers possessing significantly different reactivities. Reactivity ratios were determined for the technologically important IB–pMeSt copolymerization system. Although these reactivity ratios are reliable, they are valid only over the narrow feed composition range within which they were determined. These r values were used to simulate the macro- and micro-compositions of IB–pMeSt copolymers. These simulation results indicate that our method yields reliable reactivity ratios and can be used to describe quantitatively copolymerization behavior over a narrow but technologically significant initial feed composition range.

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