Chemical composition distribution of styrene–ethyl methacrylate copolymers studied by means of t.l.c./f.i.d.: effect of high conversion in various polymerization processes

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The chemical composition distributions (CCD) of poly(styrene–co ethyl methacrylate) copolymers obtained up to very high conversions by means of different polymerization techniques have been determined by a quantitative thin-layer chromatography/flame ionization detection (t.l.c./f.i.d.) method, using a concentration gradient elution technique for development. Under these conditions, the separation took place exclusively according to composition (molar mass ranged from 29 000 to 320 000), with a possible minor exception in the very low molar mass region ($< 35\,000$). For the evaluation of the experimental CCDs from t.l.c./f.i.d. data, a method was developed which takes into account the different molar masses of the monomers and the specific detector responses to the various copolymeric species. The model proposed for the theoretical prediction of the total CCD is based on both conversion and instantaneous CCD. The conversion CCD was calculated by a novel simple analytical expression, using formulae compatible with one of the most reliable methods of estimating r-values, i.e. the improved curve fitting I-procedure. The instantaneous CCD was calculated by means of an extended Stockmayer model, which takes into account the different molar masses of the monomer units. It is shown that for copolymers of styrene–ethyl methacrylate (sty–ema) prepared under non-azeotropic conditions the instantaneous CCD significantly affects the total CCD. The agreement found between calculated and experimentally observed CCD's was verg good for copolymers prepared to high conversion by means of the solution process. For copolymers prepared by bulk or emulsion processes significant anomalous effects were observed.

(Keywords: copolymers; high conversion batch processes; chemical composition distributions; quantitative thin-layer chromatography; flame ionization detection)

INTRODUCTION

Determination of the chemical composition distribution (CCD) of copolymers is increasingly recognized as extremely important in copolymer characterization. Compositional heterogeneity strongly affects the physical and mechanical properties of copolymers[1]. Since a comparison of the expected and observed CCDs may contribute to the elucidation of 'anomalous' reaction kinetics (e.g. high conversion emulsion copolymerization), compositional characterization is obviously of paramount importance.

Several methods have been proposed to solve the problem. Among these are solvent/non-solvent fractionation procedures[2], light scattering[3] and density gradient ultracentrifugation[4]. Despite the undeniable value of these methods in the characterization of homopolymers, two problems still remain: the laborious time-consuming experimental procedures, and the inevitable interference of the chemical composition distribution with the molar mass distribution.

A significant improvement could be achieved by the application of chromatographic techniques in which the separation is mainly governed by adsorption–desorption mechanisms. First Inagaki[5,6] and coworkers carried out the separation of styrene–methylacrylate copolymers by means of thin-layer chromatography (t.l.c.). Since that time a number of publications[5–9] have appeared on separation according to composition of other copolymers. It appeared also to be possible to separate according to stereoregularity[10].

However, the quantification of chromatograms, obtained by conventional t.l.c. has many difficulties and error sources. The visualization must be carried out very accurately, and is adversely affected by inhomogeneities on the plate. Also, hypochromic effects in the ultraviolet spectra of copolymers[11] may be operative to some extent, due to the dependency of the ultraviolet (u.v.) absorption on the styrene sequence arrangement. Moreover, the components must absorb in the visible or u.v. region.

Teremachi[12] introduced a high speed liquid chromatographic method to obtain the CCD. However, it is doubted whether this method will be generally applicable to reveal separations between copolymers exclusively according to composition, since the stationary phase is used in the unactivated state.

The t.l.c./flame ionization detection (t.l.c./f.i.d.) technique as proposed by Padley[13], however, uses an activated stationary phase and a detector based on the principle of flame ionization. As a consequence, this technique avoids all drawbacks of the above-mentioned chromatographic separation and quantification methods, and may supply direct information on the CCD. Because of the fundamental advantages of the t.l.c./f.i.d. technique, we developed an experimental method based on these principles but suited to the investigation of styrene–ethyl methacrylate copolymers.

Assuming Alfrey–Mayo (AM) kinetics, one can calculate the total CCD of copolymers. The assumption was found to be justified for many binary copolymerization systems, although some investigators cast doubt on the validity of this model under certain conditions. Disagreement between AM theory and experiment have been observed for copolymers prepared to high conversion in bulk. For example, Johnson et al.[14] and Dionisio et al.[15] reported anomalous copolymerization behaviour of the system styrene–methyl methacrylate. However, in a more recent publication O'Driscoll et al.[16] showed that the accuracy of their measurements was insufficient to prove conclusively the existence of the high conversion effect. Anomalous behaviour was reported by Kelen et al.[17] in the copolymerization of vinylidene cyanide–maleic anhydride, by Zilberman et al.[18] in the copolymerization of methacrylamide–methacrylic acid and by Tacx et al.[19] in the copolymerization of styrene and ethyl methacrylate.

Mirabella et al.[20] found for copolymers of vinylchloride and vinylstearate prepared in bulk, that the variation in composition with molar mass was significantly greater than calculated from theory. Nunes et al.[21] obtained similar results for the system styrene–methyl methacrylate initiated by ethyl aluminium-sesquichloride and Bartik[22] for styrene–acrylonitrile copolymers.

These considerations as well as the impact of CCD on copolymer properties justify our investigation on the comparison of predicted and observed CCDs of styrene–ethyl methacrylate copolymers prepared at high conversions.

EXPERIMENTAL

Purification of chemicals

The monomers styrene and ethyl methacrylate (Merck) were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. In all cases the distillate was found to be >99.5% pure by gas–liquid chromatography (g.l.c.) analysis. The free radical initiator AIBN (Fluka p.a.) was recrystallized once from methanol. The solvent toluene (Merck p.a.) was dried over sodium, degassed and distilled under helium.

Preparation of low conversion solution samples, i.e. reference copolymers

The reference copolymers, with a narrow distribution according to chemical composition, were prepared under high pressure (118 MPa) in a stainless steel autoclave (Autoclave Engineers) as described in detail elsewhere[23].

The total monomer concentration was $1 \, mol \, dm^{-3}$ in toluene; the initiator concentration was $5 \, mmol \, dm^{-3}$.

Both conversion and monomer feed ratio were calculated from monitoring of the monomer concentrations by means of g.l.c. during the entire course of the reaction. Samples of 2 μl were injected by means of a special sampling disk valve described previously[24]. The g.l.c. conditions were: stationary phase, carbowax 400 on poracil S100-120 mesh (Waters Associates Inc.); column length 1.20 m; column temperature 388 K; detector temperature 423 K; and injection port temperature 393 K. Total monomer conversions were generally less than 12%. Copolymer compositions were determined by nuclear magnetic resonance (n.m.r.), as described elsewhere[25].

Preparation of high conversion samples

Solution polymerization process. The polymerizations were carried out in a stainless steel reactor (SFS), flushed with nitrogen before use. The total monomer concentration was $3 \, mol \, dm^{-3}$, the solvent was toluene and the initial initiator concentration $5 \, mmol \, dm^{-3}$. The reaction mixtures were thermostated at 335 ± 0.2 K and stirred at 100 rev min^{-1}. The entire course of the reaction was continually monitored by g.l.c.

Bulk polymerization process. The reaction conditions were the same as applied in the solution process. The initiator concentration was $10 \, mmol \, dm^{-3}$. Other experimental details have been described elsewhere[19].

Emulsion polymerization process. The copolymer latices were prepared in a 1 l glass vessel. The monomers (300 g) were added dropwise to the soap solution (4 g sodium laurylsulphate; Merck p.a.) emulsifier and 2 g sodium carbonate (Merck p.a. dissolved in 1000 g distilled water). Subsequently, a potassium persulphate (Merck p.a.) solution (2 g dissolved in 25 ml distilled water) was added to the reaction mixture, thermostated at 335 ± 0.3 K. Total weight conversion was determined by solid content analysis. The feed ratio was calculated from monitoring monomer ratios by means of g.l.c. The g.l.c. conditions were: 10% polyphenyl ether 60-80 W 700: column length 183 cm; column temperature 423 K; detector temperature 473 K; injection port temperature 423 K.

Working-up procedure for the products. All copolymers prepared by means of the solution and bulk processes were isolated and purified by pouring out in cold hexane. The final products were dried at 328 K in a vacuum oven for 6 h at 10^{-1} torr and finally for 8 h at 10^{-5} torr. (Some copolymers were also recovered by solvent evaporation under reduced pressure. These showed identical CCD results within experimental error.)

The copolymers obtained by emulsion copolymerization were purified from emulsifier, unreacted initiator and monomers by careful coagulation with an aluminium nitrate (Fluka) solution (0.001 $mol \, dm^{-3}$), subsequent decantation and filtration of water and coagulant.

The final products were thoroughly washed with boiling water and dried at 10^{-5} torr for at least 8 h.

Molar mass

The number average molar mass (M_n) of the styrene–ethyl methacrylate copolymer samples was determined in toluene using a Hewlett Packard high speed membrane osmometer, model 502.

Conventional and automated quantitative t.l.c.

To find suitable experimental conditions for the t.l.c./f.i.d. investigation, preliminary separation tests were carried out, using conventional t.l.c. plates. Before use the silica plates (Merck, A.G. Darmstadt) were activated at 408 K for 15 min. Stock solutions of copolymers were prepared (15 g dm^{-3}) in toluene. Each initial spot on the plate contained 15 μg of copolymer. In contrast to conventional t.l.c. spotting procedures, the spotted plates were not dried before elution. This anomalous procedure was chosen to prohibit precipitation of the copolymer on the silica surface. In this manner, the copolymer remains in equilibrium with the solvent and adsorbent, thus avoiding slow re-dissolution of copolymer during the gradient elution. Such interference caused by re-dissolution would otherwise yield an apparent CCD. Moreover, for 30 min the spotted plate was placed in a vessel saturated with vapour of the initial eluent, to reach equilibrium. The gradient elution was performed, using toluene as the non-polar solvent and acetone or methylethylketone as the polar solvent. As soon as the eluent front reached the starting point, appropriate aliquots of polar solvent were added at predetermined intervals until the eluent front reached 10 cm ahead of the starting level. The migration was stopped by removing the plates from the vessel and evaporating the eluent by a hot air stream. The positions of the final spots were visualized by exposure to u.v. light or iodine vapour.

When the appropriate t.l.c. conditions were established from the plate experiments, the more sophisticated t.l.c./f.i.d. method was applied for direct quantitative analysis. The t.l.c./f.i.d. separations were performed on quartz rods (Iatron Chromarod S-I). With a microsyringe, a spot of the stock solution (0.1 μl), containing 1.5 μg copolymer, was deposited at the starting level of the rods. After development under conditions comparable with those determined during the plate experiments, the rods were dried and transferred to the scanning apparatus equipped with an f.i.d. (commercially available equipment: Iatroscan TH-10, Mark-III) for direct quantitative analysis. The electronic f.i.d. amplifier of the Iatroscan was replaced by a Keithley high speed picoammeter, model 417. This modification appeared to improve the linearity and sensitivity significantly, as required for our analysis.

RESULTS AND DISCUSSION

Evaluation of theoretical CCD

During most batch copolymerization processes, the monomer feed ratio inevitably shifts as conversion increases. This well known phenomenon gives rise to the so-called conversion heterogeneity. The instantaneous heterogeneity, due to the finiteness of the chain length and the statistical character of the addition process, also contributes to the total heterogeneity[28]. Moreover, anomalous kinetics (for instance, defined as deviating from the Alfrey–Mayo (AM) model) may introduce an additional heterogeneity according to chemical composition.

The total heterogeneity of copolymers exhibiting AM kinetics can be calculated by taking into account both conversion and instantaneous heterogeneity. For the calculation of conversion heterogeneity, a simple analytical expression is presented using mathematical equations, which in form are compatible with an advanced and reliable method of estimating r-values, i.e. the improved curve fitting I-procedure[24,26,27]. The instantaneous heterogeneity may be calculated by the Stockmayer model[12,28,29]. However, this model is only valid for systems with monomers of equal molar masses. Since most binary monomer combinations have different molar masses, Tacx et al.[30] proposed an extension of the Stockmayer model, which takes into account the proper molar masses of the monomer units. Application of this extension appeared to be a necessity in the present case, since the molar masses differ by about 10%.

The total heterogeneity of a copolymer, prepared in a high conversion experiment, can be described by a differential weight distribution function $f_t(x_i)$, according to

$$f_t(x_i) = (1/C_{we}) \int_{C_w} f_s'(x_i \mid \bar{x}) \, dC_w \qquad (1)$$

where x_i is the mole fraction of monomer 1 (M_1) in the copolymer, $\bar{x}$ is the average composition (mole fraction of M_1) of the copolymer, C_w is total weight conversion and subscript e indicates final conditions. C_{we} may be regarded as a normalization factor and $f_s'(x_i \mid \bar{x})$ is the modified (differentiation of monomer molar masses)[30] Stockmayer differential weight distribution function, given by

$$f_s'(x_i \mid \bar{x}) = f_s(x_i \mid \bar{x}) \left[1 + \frac{y(1-k)}{k + \bar{x}(1-k)} \right] \qquad (2)$$

where $f_s(x_i \mid \bar{x})$ is the original Stockmayer distribution function[28].

Equation (1) may be rewritten by introducing $d(C_w/C_{we}) = dI_w$ and $f_c = (dI_w/d\bar{x})$:

$$f_t(x_i) = \int_{\bar{x}} f_s'(x_i \mid \bar{x}) |f_c(\bar{x})| \, d\bar{x} \qquad (3)$$

Here I_w is the integral weight fraction of copolymer and f_c is the differential weight distribution function, describing the conversion heterogeneity.

The function $f_c(x)$ may be calculated numerically[31] as done by Ogawa[32]. However, it is worthwhile to derive an analytical expression for the conversion heterogeneity, thus avoiding time-consuming iterative estimation of this derivative. The main lines of the derivation will be presented here. The function f_c can be rewritten as

$$f_c(\bar{x}) = \frac{dI_w}{d\bar{x}} = \frac{dI_w}{dq} \frac{dq}{d\bar{x}} \qquad (4)$$

where q is the molar feed ratio ($[M_1]/[M_2]$) of the monomers. The integral weight fraction of copolymer is mathematically expressed by

$$I_w = \frac{\text{conv } M_1 q_0 T + \text{conv } M_2}{\text{conv } M_{1e} q_0 T + \text{conv } M_{2e}} \qquad (5)$$

In this equation conv M_i is the molar conversion of M_i and T is the molar mass ratio (M_1/M_2). Furthermore, the
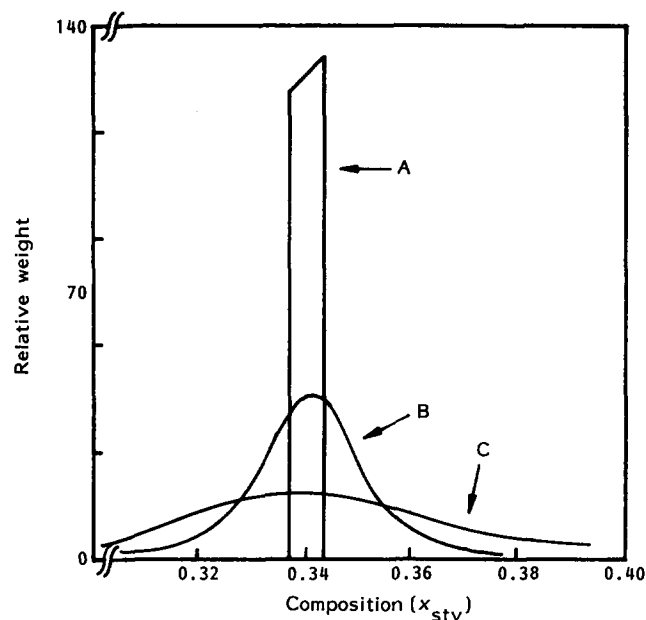
Figure 1 Effect of molar mass on CCD of sty–ema copolymers: A, $M_n = \infty$; B, $M_n = 100\,000$; C, $M_n = 10\,000$. Initial feed ratio, 0.33; total mole conversion, 1%
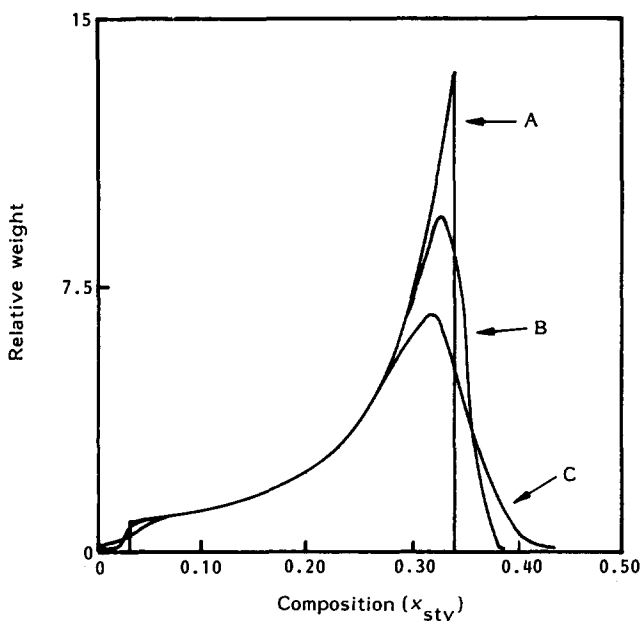

Figure 2 Effect of molar mass on CCD of sty–ema copolymers: A, $M_n = \infty$; B, $M_n = 100\,000$; C, $M_n = 10\,000$. Initial feed ratio, 0.33; total mole conversion, 98%. The scales of *Figures 1* and *2* are different to reveal important details

following equation is valid:

$$Z_i = 1 - \text{conv } M_i \tag{6}$$

According to the principles of mass balance one can easily obtain

$$Z_1 = (q/q_0)Z_2 \tag{7}$$

$$Z_t = [(q+1)/(q_0+1)]Z_2 \tag{8}$$

where subscript t indicates total molar conversion. Z_2 is expressed as a function of q according to the integrated AM model:

$$Z_2 = (q/q_0)^{-x_2-1}\left[\frac{x_2 q - x_1}{x_2 q_0 - x_1}\right]^{1+x_1+x_2}$$

where $x_i = (1 - r_i)^{-1}$.

By substituting equations (6)–(8) into equation (5) and differentiating (5) with respect to q, the following equation is obtained:

$$\frac{dI_w}{dq} = -Z_2\left[\frac{-1-x_2}{q} + \frac{x_2(1+x_1+x_2)}{qx_2-x_1} + \frac{T}{1+qT}\right]$$
$$\times \left[\frac{1+qT}{-Z_{2c}(1+qT)+(1+q_0 T)}\right] \tag{9}$$

By differentiating the simple copolymer equation of Alfrey and Mayo

$$\bar{x} = \left[1 + \frac{r_2/q+1}{r_1 q + 1}\right]^{-1}$$

with respect to q, the following equation is obtained:

$$\frac{dq}{d\bar{x}} = \frac{-[(r_1 q + 1) + (r_2/q + 1)]^2}{[(r_1 q + 1)(r_2/q^2)] - [r_1(r_2/q + 1)]} \tag{10}$$

Fast numerical integration of equation (3) now becomes possible since the integrand is analytically expressed as a product of three functions.

The differential weight distribution function, i.e. the total CCD, due to both instantaneous CCD and conversion CCD is now described by a plot of $f_t(x_i)$ versus x_i. This curve should correspond to the composition curve obtained from t.l.c./f.i.d. for copolymers exhibiting AM kinetics and prepared by means of batch solution polymerization. The effect of instantaneous and conversion CCD on the total CCD is demonstrated in *Figures 1* and *2*. It appears that even at high conversions and high molar mass, the instantaneous CCD (varies by changing copolymer molar mass) significantly affects the total CCD.

Determination of r-values

The r-values are extremely important parameters in the calculation of compositional heterogeneity. As a consequence, accurate and precise estimation of r-values is imperative. G.l.c. analysis of the reaction mixture throughout a copolymerization reaction in conjunction with the improved curve fitting I-procedure[23,24,26,27], which accounts for measurement errors in both variables, has been found to lead to a reliable estimation of monomer reactivity ratios[23,33]. Therefore, this procedure was also adopted in the present investigation. The results are given in *Table 1*.

Within experimental error, the values obtained from low pressure (0.1 MPa) experiments are in agreement with values reported in the literature[34]. Reactivity ratios obtained at high pressure have not been reported to date. These r-values follow the tendency found in many systems[26], namely a shift of the product of r-values toward unity (i.e. toward more ideal copolymerization behaviour) as pressure increases.

Table 1 Reactivity ratios of sty (r_1) and ema (r_2) at 335 K in different media and at different pressures

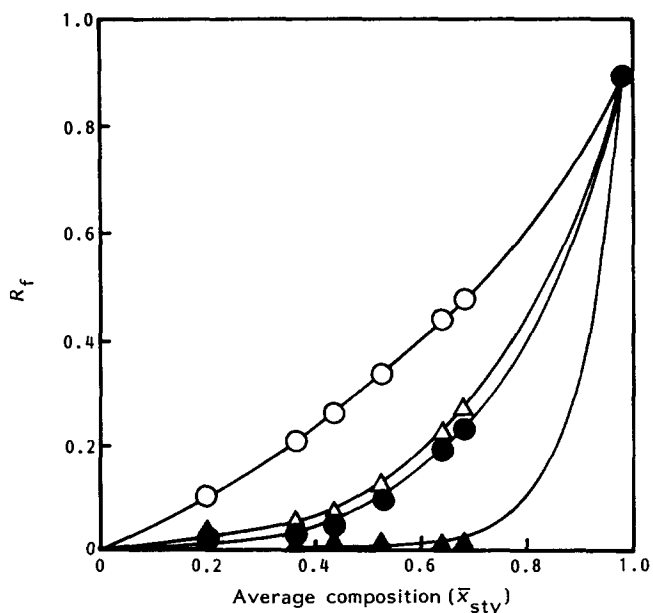| Medium	Pressure (MPa)	r_1	r_2
Bulk	0.1	0.46 ± 0.03	0.38 ± 0.04
Toluene	0.1	0.49 ± 0.02	0.40 ± 0.03
Toluene	118	0.59 ± 0.03	0.50 ± 0.02

Figure 3 Experimental results for R_f *versus* copolymer composition (mole fraction styrene) under various elution conditions: ○, △, 100 ml toluene, at solvent front positions of 2.5, 5, 7.5 cm, 2.5, 5, 7 ml acetone, respectively, have been added successively. ●, ▲, 100 ml toluene, at solvent front positions of 2.5, 5, 7.5 cm, 3.0, 2.0, 1.0 ml acetone, respectively, have been added successively. △, ▲, Chromarod; ○, ●, chromatoplate

Table 2 Dependence of R_f on molar mass

M_n	R_f	Ema concentration (mol%)
270 000	0.32	32.5
79 000	0.34	31.7
40 000	0.31	31.9
29 000	0.34	32.3

Choice of developers

Since the adsorption–desorption mechanism has to be operative to obtain the desired separation of copolymers according to chemical composition, the developers must behave as good solvents. For this purpose several solvents were tested. However, no single solvent or constant mixture of solvents was capable of separating all copolymers with compositions ranging from 20 to 69% sty. The best results were obtained when applying a concentration gradient technique with toluene as the nonpolar solvent and methylethylketone (MEK) or acetone as the secondary polar solvent. The results of the t.l.c. separations under varying conditions on conventional plates and on rods are presented in *Figure 3*.

From these results it appears that under the same elution conditions the chromatographic behaviour of copolymers on conventional plates differs from that on chromarods. A higher activity of the stationary phase of the rods forms a plausible explanation of this phenomenon.

Dependence of R_f on molar mass

The desired separation according to chemical composition can most easily be achieved in the absence of any interference caused by molar mass variations. To determine any possible molar mass dependency of

R_f-values, several copolymers were prepared with approximately the same overall composition but different molar masses. Characteristics of the samples are given in *Table 2*. As shown in *Figure 4*, R_f-values are practically independent of molar mass with a possible exception in the very low molar mass region.

Evaluation of experimental CCD of copolymers

The t.l.c. chromatograms were converted into differential weight distributions according to a method we described elsewhere[35]. The characteristics of the low conversion reference copolymers used to set up a calibration curve, i.e. a relation between R_f and copolymer composition, are summarized in *Table 3*. The chromatogram of an arbitrarily investigated copolymer now can be converted into an experimental CCD by means of the calibration curve and correction of the signal as explained elsewhere[35].

The observed experimental CCD and the calculated theoretical CCD of the reference copolymer S-38 are shown in *Figure 5*.
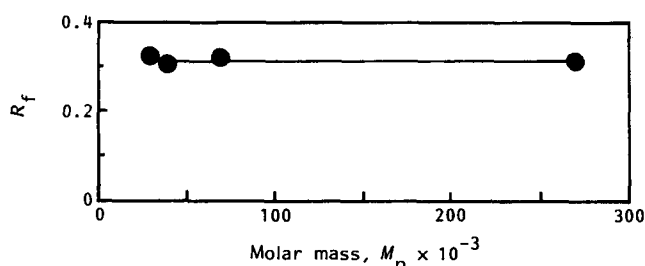

Figure 4 Dependence of R_f on molar mass at constant polymer composition, ≈0.68 mole fraction sty

Table 3 Characteristics of reference copolymers

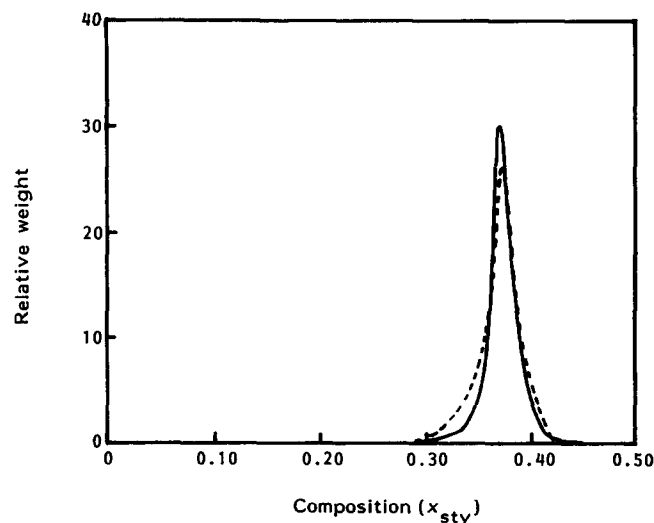| Number	Sty concentration (mol%)	Molecular mass M_n
S-69	69	46 000
S-65	65	46 000
S-52	52	48 000
S-42	42	48 000
S-38	38	50 000
S-20	20	47 000

Figure 5 Chemical composition distribution of a low conversion reference copolymer S-38: ——, predicted; – – –, observed CCD
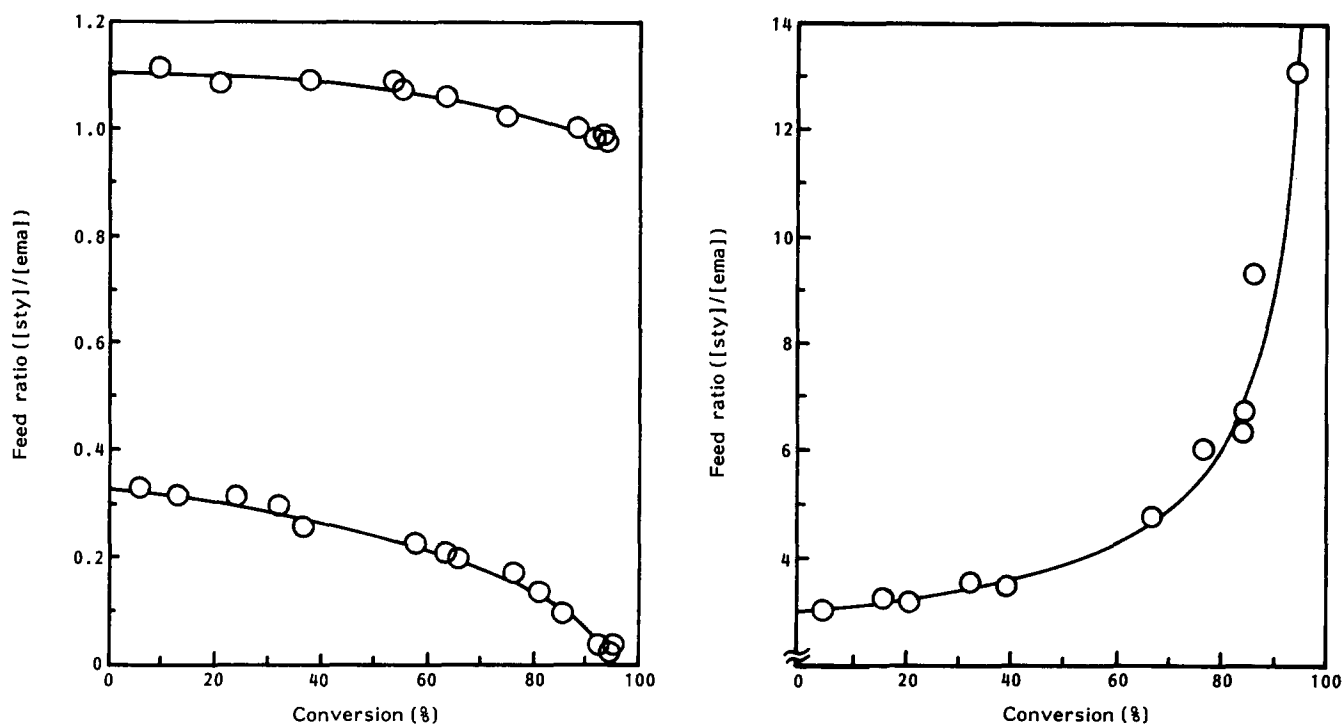
Figure 6 ○, Observed and, ——, predicted feed ratio conversion relation ($r_1 = 0.49$, $r_2 = 0.40$) of sty and ema in toluene
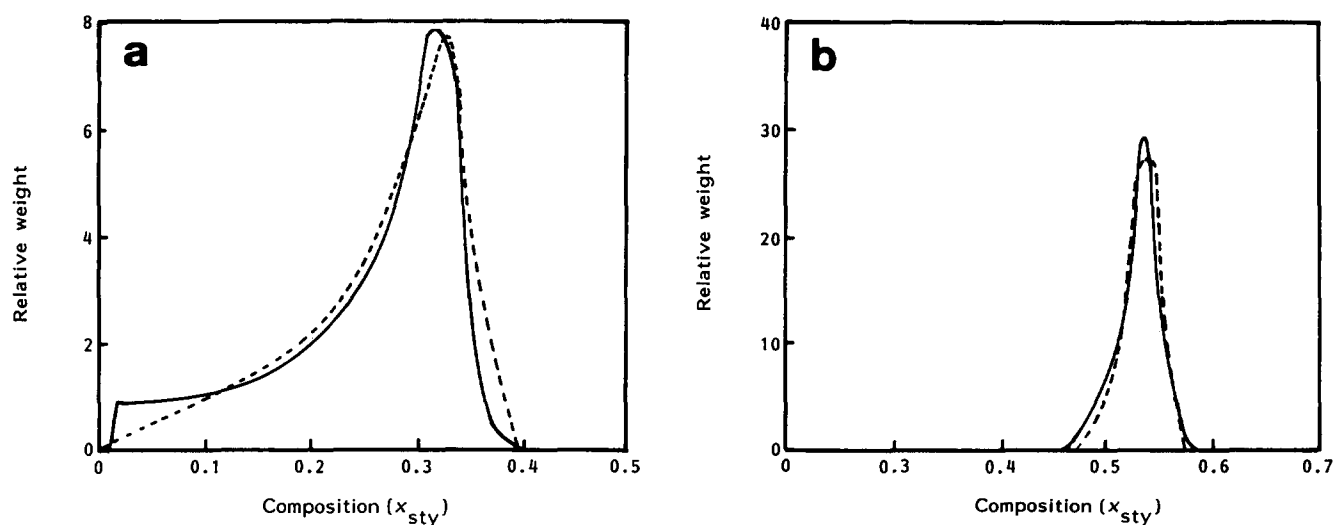

Figure 7 Chemical composition distribution of two copolymers obtained at high conversion (98 mol %) in solution: (a) $q_0 = 0.33$; (b) $q_0 = 1.1$. ——, Predicted; –––, observed CCD

The copolymerization kinetics of sty and ema in dilute solutions can be successfully described by means of the classical AM model[19]. So the heterogeneity can be predicted from the well known AM kinetics in conjunction with the extended Stockmayer model[30] according to the above-mentioned mathematical procedures. From *Figure 5* it appears that the agreement between the predicted CCD based both on compositional drift and random addition statistics, and on the observed CCD of the low conversion copolymer S-38 is surprisingly good. So it may be concluded that the CCD of copolymers can be successfully determined by means of the t.l.c./f.i.d. technique. Obviously, the chromatographic separation procedure itself adds no significant peak broadening, even compared with the width of the compositional distribution of a low conversion copolymer.

As a consequence, it may be inferred that where an observed CCD differs significantly from the predicted one, the cause can be almost exclusively attributed to the occurrence of anomalous copolymerization kinetics. This is because no significant dependency on molar mass was observed and the chromatographic separation causes negligible peak broadening.

The observed heterogeneities of the copolymers prepared by means of the solution process up to very high conversions (98 mol %, $q_0 = 1.1$ and $q_0 = 0.33$) are expected to be in very good agreement with those predicted, due to the absence of anomalous kinetics. This expectation could be verified from kinetic data, since the high conversion copolymerization behaviour can be successfully predicted on the basis of the r-values determined at low conversions (see *Figure 6*). The results are given in *Figure 7*. It should be emphasized that for
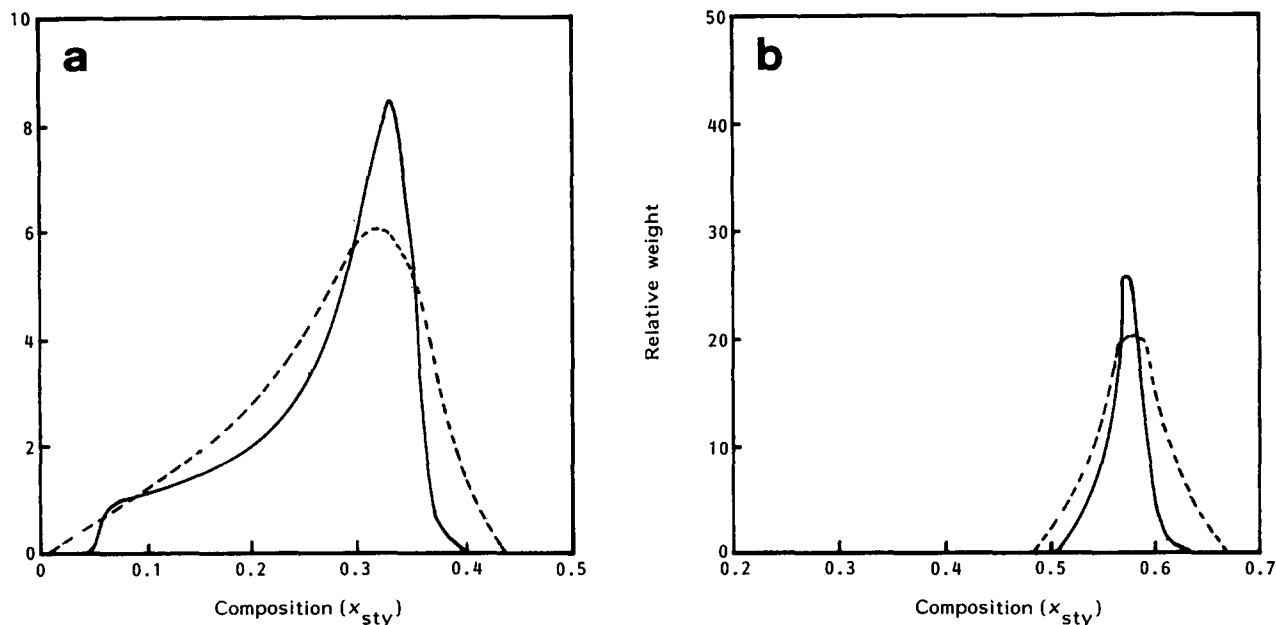
Figure 8 Chemical composition distribution of two copolymers obtained at high conversion (92 mol%) in bulk: (a) $q_0 = 0.33$; (b) $q_0 = 1.1$. ——, Predicted; ———, observed CCD
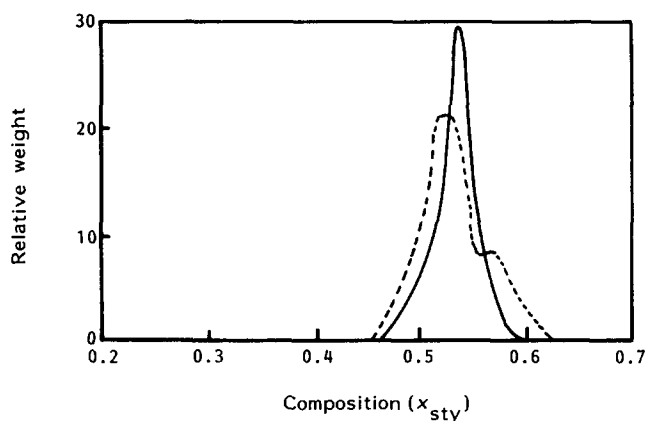

Figure 9 Chemical composition distribution of a copolymer obtained at high conversion (95 mol%) in emulsion, $q_0 = 1.1$: ———, predicted; ———, observed CCD

nearly azeotropic copolymerization (here $q_0 = 1.1$) the instantaneous CCD mainly determines the total CCD, regardless of the degree of conversion.

On the other hand, the total observed heterogeneity of a copolymer prepared at very high conversions (92%, $q_0 = 1.1$ and $q_0 = 0.33$) by means of the bulk process differs significantly from the predicted heterogeneity (see *Figure 8*). This must be attributed to the occurrence of anomalous copolymerization kinetics, probably due to a shift in the value of the (apparent) kinetic parameters with the conversion[19]. The results are presented in *Figure 8*.

For copolymers prepared in an emulsion process to very high conversions (95%, $q_0 = 1.1$), striking discrepancies are observed between observed and predicted product distributions. These copolymers exhibit a very broad or even a bimodal experimentally observed product distribution. The results are presented in *Figure 9*. From these results, it might be inferred that besides the expected polymerization in the reaction loci, propagation reactions must also take place at other places within the intrinsically heterogeneous emulsion system.

Any interference caused by emulsifier bound to the polymer chains, which during separation might lead to anomalous CCDs[36], must be ruled out in our case, since the overall compositions obtained by t.l.c. and n.m.r. are in full agreement. Furthermore, only a negligible amount of polymer remained on the starting level and no strong tail toward the starting level was observed.

So it may be concluded that the observed CCD practically coincides with the actual copolymer product distribution. These striking results presented in *Figure 9*, which cannot be predicted by means of conventional AM kinetics, may provide important information to improve kinetic models describing high conversion bulk and emulsion polymerization. For instance, the present results seem to indicate that a second mechanism is operative during the course of the batch emulsion copolymerization of sty with ema.

CONCLUSIONS

The results of the present investigation indicate that the calculation method, which takes into account both instantaneous CCD (extended Stockmayer model) and conversion CCD (analytical expression compatible with improved curve fitting I-procedure), leads to a reliable estimation of the total CCD of copolymers prepared by means of radical solution processes exhibiting AM kinetics. It appears that even for non-azeotropic copolymerization up to rather high conversions, the instantaneous CCD significantly affects the total CCD.

Furthermore, the t.l.c./f.i.d. method proved to be a very powerful tool in determining the total CCD for the system styrene–ethyl methacrylate.

A comparison of the experimentally observed and theoretically expected total CCDs indicates that the product distribution strongly depends on the type of polymerization process applied in preparing the copolymers.

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