Determination of molar-mass chemical-composition distribution in copolymers by cross-fractionation, based on size exclusion chromatography and thin-layer chromatography/flame ionization detection

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The molar-mass chemical-composition distribution (MMCCD) of poly(styrene-co-ethyl methacrylate) copolymers, obtained till low and high conversions by a batch solution polymerization technique, has been determined by a new cross-fractionation method. In this method, the copolymers are first separated according to hydrodynamic volume by size exclusion chromatography (molar mass) and fractions are subsequently analysed by quantitative thin-layer chromatography/flame ionization detection according to composition. For the evaluation of the experimental MMCCD, a method was developed that takes into account the various detector responses to the copolymers. The semiquantitative model proposed for the prediction of the total MMCCD is based on the instantaneous and conversion kinetics. It was shown that for copolymers, even those prepared under non-azeotropic conditions, the instantaneous MMCCD significantly affects the total MMCCD. The predicted and observed MMCCDs were in favourable agreement for copolymers obtained by low- and high-conversion batch solution processes, confirming the reliability of the experimental techniques and the semiquantitative model.

(Keywords: molar-mass chemical-composition; copolymers; size exclusion chromatography; thin-layer chromatography; flame ionization detection)

INTRODUCTION

Copolymers usually possess a very complex chain architecture, i.e. microstructure. Molecules of copolymers may differ in the configurational orientation of the side groups, in sequence-length distribution and in molar-mass chemical-composition distribution (MMCCD). The latter, a two-dimensional distribution, is caused by the simultaneously occurring molar-mass and chemical-composition distributions (MMD and CCD) in copolymers.

Revelation of the MMCCD of copolymers is important from two points of view. The process kinetics determines the MMCCD, which in turn determines the properties of the copolymers. So, fundamental knowledge about the MMCCD may not only supply information about the kinetics but may also contribute to a better understanding of relations between material properties and microstructure. This explains why the experimental determination of MMCCD is increasingly recognized as a prime goal in copolymerization.

Despite its paramount importance, a standard technique to characterize copolymers simultaneously according to molar mass as well as to chemical composition is not available. However, in some selected cases it appeared to be possible to fractionate copolymers separately according to molar mass or chemical composition.

However, the most powerful method of revealing the combined MMD and CCD is cross-fractionation.

This procedure requires fractionation according to one property ('in one direction') and subsequent separation of the fractions according to the second property; the separation characteristics should be as independent as possible. Several methods have been proposed to determine the molecular structure (MMCCD) of copolymers by means of cross-fractionation, e.g. solvent/non-solvent fractionation procedures and crystallization fractionation with subsequent analysis by means of size exclusion chromatography (s.e.c.). Using classical techniques these experimental methods are laborious and time-consuming and require the often troublesome search for suitable solvent/non-solvent pairs.

A significant improvement was achieved by application of chromatographic techniques. For instance, Inagaki carried out cross-fractionation experiments by combining column adsorption chromatography with s.e.c., and Taga applied thin-layer chromatography (t.l.c.) with s.e.c. Especially a combination of s.e.c. with subsequent analysis appeared to be very attractive. Hoffmann used s.e.c. with turbidimetry; Balke used two s.e.c.'s to reveal the MMCCD; Glöckner successfully combined s.e.c. with high-performance precipitation liquid chromatography (h.p.p.l.c.); and Belenkiij and Teremachi used s.e.c. with classical t.l.c.

It became apparent that especially t.l.c. has specific advantages, i.e. the separation might be arranged in such a fashion as to occur exclusively according to composition. However, the quantification of chromatograms obtained by conventional plate t.l.c. is accom-
panied by many difficulties. The visualization must be carried out very accurately and is adversely affected by inhomogeneities on the plate. Moreover, the components must absorb in the visible or u.v. region.

The thin-layer chromatography/flame ionization detection technique, as proposed by Padley, uses a detector based on the principles of flame ionization detection (f.i.d.). As a consequence, this technique avoids all drawbacks of the above-mentioned classical t.l.c. quantification and supplies direct information about the CCD.

As a result, from earlier investigations, we have found that copolymers of styrene and ethyl methacrylate could be successfully separated, practically exclusively according to composition, by application of t.l.c. with a concentration gradient technique for development. Moreover, the t.l.c./f.i.d. method requires approximately 1 μg of copolymer, in contrast to classical t.l.c. quantification techniques that need nearly 15 times more.

These considerations, as well as the expected capability of experimental MMCCDs to reveal relations between process kinetics and material properties, justify our investigation on the feasibility of s.e.c. and t.l.c./f.i.d. as a cross-fractionation method.

EXPERIMENTAL

Purification of chemicals

The specifications of the monomers, styrene (Sty) and ethyl methacrylate (EMA), and the radical initiators, azobisisobutyronitrile (AIBN) and potassium persulphate, have been described elsewhere.

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

The synthesis of the reference copolymers has been described in detail elsewhere.

Preparation of high-conversion samples

The copolymer latex was prepared using a 1 litre glass vessel. The monomers (300 g), in which 2.1 g n-dodecylmercaptan was dissolved, were pre-emulsified by adding them to the emulsifier solution (3.9 g sodium laurylsulphate (SLS) (Fluka) in 700 g water distilled twice). Finally, the radical initiator, potassium persulphate (2 g), dissolved in 20 g distilled water, was added to the monomer emulsion. The reaction mixture, stirred at 200 rpm, was thermostated at 335±0.3 K.

Total weight conversion was determined by solid content analysis. The product was immediately worked up, according to a procedure described elsewhere.

The preparation of the high-conversion solution samples has been described in earlier work.

Analysis

Size exclusion chromatography. S.e.c. was performed on a Waters chromatograph (Waters Associates) connected to a differential refractometer and an ultra-violet (u.v.) detector (254 nm). The s.e.c. column set consisted of 102, 103, 104, 105 Å μ-Styragel columns. Calibration was performed using 10 polystyrene samples with a narrow molar-mass distribution (MMD).

For cross-fractionation experiments, a 1000 μl sample volume of 0.1% (w/v) concentration was injected onto the columns. The solvent flow rate was set at 0.9 ml min⁻¹. Tetrahydrofuran (THF) was used as the mobile phase. All fractionation experiments were carried out at 292 K. The solvent (THF) of each fraction (1.5–3 ml solution) was evaporated by a nitrogen flow. Subsequently, the remaining polymer was redissolved under nitrogen in 40–150 μl toluene by shaking for at least 6 h.

Thin-layer chromatography. In order to find the required conditions in the t.l.c./f.i.d. separations, preliminary experiments were carried out using a conventional plate. After the appropriate conditions were established from plate experiments the more advanced t.l.c./f.i.d. method was applied for direct quantitative analysis. Details on the spotting and elution procedures, which differ considerably from those used in the conventional separation of low-molar-mass components, have been described elsewhere.

Data treatment

All chromatograms were digitized using a Callcomp 100 digitizer. The calculations were carried out on a Burroughs B7900 main frame computer.

RESULTS AND DISCUSSION

Evaluation of theoretical MMCCD

During a copolymerization reaction, the MMD and CCD occur simultaneously, resulting in a two-dimensional distribution called MMCCD, i.e. molar-mass-chemical-composition distribution. Stockmayer derived differential weight distribution functions to describe the MMCCD of the instantaneously formed product, assuming equal molar masses of the monomeric units. We have generalized this model, now including binary systems with unequal molar masses.

However, during a high-conversion batch solution copolymerization, the instantaneous MMCCD commonly changes as conversion increases. During our experiments, the instantaneous molar mass was kept constant by adjusting the initiator concentration. So, the MMCCD of the resulting copolymer can be calculated by integration with respect to the conversion of the instantaneous MMCCD according to equation (1), assuming the degree of polymerization to be independent of conversion:

\[ f_I(x_i, P_w) = \int f_S(x_i, P_i | \bar{x}, P_w) \, dc_w \]  

(1)

Here, \( x_i \) is the mole fraction of monomer \( i \) of an arbitrarily chosen composition and \( \bar{x} \) is the average composition of the instantaneously formed product. Similarly, \( P_w \) is an arbitrarily chosen degree of polymerization and \( \bar{P}_w \) is the number-average degree of polymerization. The total weight conversion is given by \( c_w \) and subscript \( e \) indicates final conditions. The factor \( c_{we} \) may be regarded as a normalization constant and \( f_S(x_i, P_i | \bar{x}, P_w) \) is the extended (with respect to variations in molar masses of the monomeric units) Stockmayer differential weight distribution function given by:

\[ f_S(x_i, P_i | \bar{x}, P_w) = f_S(x_i, P_i | \bar{x}, P_w)[1 + (cy(1-k))/[(k + \bar{x}(1-k))]] \]  

(2)

where \( f_s \) is the original differential weight distribution derived by Stockmayer, \( y \) is the composition deviation.
from the average value and \( k \) is the ratio of molar masses of the monomers, i.e. \( k = M_2/M_1 \).

It has been shown\(^{24} \) that equation (1) can be rewritten as:

\[
f_i(x_i, P_i | \tilde{x}, \tilde{P}_n) = \int f_i'(x_i, P_i | \tilde{x}, \tilde{P}_n)(dI_w/dq)(dq/d\tilde{x}) d\tilde{x}
\]

(3)

Here \( I_w \) is the integral weight fraction of copolymer and \( q \) is the instantaneous molar feed ratio, i.e. \( q = [\text{Sty}] / [\text{EMA}] \). In equation (3) the product \([dI_w/dq](dq/d\tilde{x})]\) may be regarded as a statistical weight function indicating the relative weight of each instantaneously formed product. This function consists of a product of two derivatives, which can be expressed analytically\(^{24} \). The first one is the derivative of the integral Alfrey–Mayo (AM) equation\(^{28} \) and the second one is the derivative of the differential AM equation. Some results of the calculations are presented in Figures 1a–c, in which distributions are presented of copolymers obtained at 1%, 80% and 98% conversion. The initial feed ratio was \( q_0 = 0.33 \), the \( r \) values \( r_1 = 0.49 \) and \( r_2 = 0.40 \) and \( P_n = 400 \). The fraction of radicals terminating by combination (\( \rho \)) was assumed to be zero.

When those distributions have to be presented in a plane of \( x_i \) and \( 10 \log M_i \), instead of \( x_i \) and \( P_i \), it is necessary to transform the distribution. This transformation\(^{29} \) can be carried out by taking into account that an infinitesimally small volume \( (Ax_i, A10 \log M, f_i(x_i, P_i)) \) contains the same relative weight of copolymer as compared with the volume \( (Ax_i, 10 \log M_i, f_i'(x_i, 10 \log M_i)) \), the result being:

\[
f_i'(x_i, 10 \log M_i) = f_i'(x_i, P_i)(M_i \ln 10)[M_2 + x_i(M_1 - M_2)]
\]

(4)

In Figures 1d–f the same distributions as presented in the series 1a–c are given on logarithmic scale, whereas in Figures 1g–i the contours of the distributions are presented. From these results it becomes immediately evident that the instantaneous distribution cannot be neglected even at high conversion. Also, as a result of a shift of the feed ratio \( q \) towards lower values, the distribution becomes asymmetric. These interesting results of the present semiquantitative model calculations will be a valuable tool in checking the validity of experimental techniques by comparing the predicted and observed MMCCDs.

**Data treatment**

In case of a homopolymer, the differential weight distribution function is calculated by measuring the elution time, and subsequent transformation to log molar mass by means of a calibration curve according to:

\[
\frac{dW}{d\log M} = \frac{dW}{dV_e} \frac{dV_e}{d\log M}
\]

(5)

where \( W \) is the weight of copolymer and \( V_e \) is the elution volume. \( (dW/dV_e) \) is the measured signal, which is proportional to the weight of homopolymer and \( (dV_e/d\log M) \) is the gradient of the calibration curve.

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**Figure 1**

(a)–(c) Predicted two-dimensional distribution of Sty–EMA copolymers according to degree of polymerization and chemical composition obtained at (a) 1%, (b) 80% and (c) 98% conversion. Parameters used: number-average degree of polymerization \( P_n = 400 \), \( r_1 = 0.49 \), \( r_2 = 0.40 \).

(d)–(f) Same two-dimensional distribution as in (a)–(c), but presented according to log molar mass and chemical composition. (g)–(i) Contours of the distributions (d)–(f)
However, in the case of a copolymer, the data treatment is much more complex. The measured signal \( S \) of the u.v. detector connected to the s.e.c. columns is given by equation (6), assuming the Lambert-Beer law to be valid:

\[
S = \frac{(dM/dV_e)}{[I_1x_1 + I_2(1-x_1)]}
\]

Here \( M \) is the molar concentration of absorbing monomeric units, \( I \) is the optical path length of the cuvette and \( \varepsilon_i \) the molar extinction coefficient of monomer \( i \) and \( x_i \) the mole fraction of styrene. By substituting \( (dM/dV_e) = (1/M)(dW/dV_e) \), in which \( M \) is the average molar mass of the monomers and \( W \) is the weight of monomers and hence polymer, in equation (6), in the case of a copolymer equation (5) becomes:

\[
\frac{dW}{d \log M} = S \frac{dV_e}{d \log M} \left[ I_1x_1 + I_2(1-x_1) \right]
\]

The composition at any elution volume is calculated from the compositional data of each fraction obtained from t.l.c./f.i.d. The calculation of the composition of each fraction from t.l.c. is outlined below.

The measured signal is related to the differential weight distribution (CCD) in a similar way as in the case of s.e.c. The CCD can be expressed according to:

\[
\frac{dW}{dx} = \frac{dW}{dR_f} \frac{dR_f}{dx}
\]

where \( dW/dx \) is the unnormalized differential weight distribution and \( dR_f/dx \) the gradient of the calibration curve. In the case of homopolymers \( dW/dR_f \) is proportional to the measured signal \( S \). For copolymers the signal is also related to \( dW/dR_f \) but in a more complex way. Assuming additivity of the signals of both types of monomers, the total measured signal can be thought to consist of two signals \( S_1 \) and \( S_2 \) due to ionization of monomers 1 and 2:

\[
S = S_1 + S_2 = c_1W_1(dW_1/dR_f) + c_2W_2(dW_2/dR_f)
\]

where \( c_i \) is the calibration constant expressed in \( \text{g}^{-1} \) and \( W_i \) the weight of monomers 1 and 2. Equation (9) can be rewritten as:

\[
S = (c_1w_1 + c_2w_2)(dW/dR_f)
\]

where \( w_i \) is the weight fraction of monomer \( i \). When the calibration constants are expressed in \( \text{mol}^{-1} \), the CCD is related to the measured signal according to:

\[
\frac{dW}{dx} = S[M_1x_1 + M_2(1-x_1)]
\]

The average composition is calculated according to:

\[
\bar{x} = \frac{\sum_{i=1}^{N} \Delta w_i(dW/dR_f)_i w_i}{\sum_{i=1}^{N} \Delta w_i(dW/dR_f)_i}
\]

Each fraction is collected between two successive elution times and hence two log molar masses. From the normalized molar-mass distribution calculated according to equation (7) the relative weight of each fraction is known. In the case of the two-dimensional distribution, the molar-mass interval as well as the CCD of each fraction are known. The height of each fraction is now proportionally adjusted to such an extent that, in the spatial representation, the relative volume of each fraction has the same value as the relative area in the planar case. This experimental set-up appeared to be necessary since quantitative spotting of the rods is not possible within the required limits of accuracy. By means of the procedure presented, a two-dimensional distribution according to molar mass and chemical composition can be obtained from s.e.c. and t.l.c./f.i.d. data.

Solvent gradient

T.l.c. separation exclusively according to chemical composition can only be achieved when the adsorption-desorption mechanism is operative. So, the developers have to behave as true solvents in order to avoid other mechanisms. Previously, we reported that the best separation results were obtained when applying a concentration gradient elution technique for development with toluene as the non-polar solvent and acetone or methyl ethyl ketone as the secondary polar solvent.

In order to find suitable elution conditions, several gradients were investigated. Some of the results are given in Figure 2. From this figure it can be seen that the shape of the gradient significantly affects the shape of the calibration curve of the reference copolymers. It appears that when the initial concentration of polar solvent is
enhanced, the copolymers having a relatively high EMA concentration show up at higher \( R_f \) values (concave calibration curve). Also, when the concentration is decreased or when the secondary polar solvent is added relatively 'late', some copolymers tend to remain at the starting level (convex calibration curve). All these observations are in agreement with a behaviour that might be expected when assuming an adsorption–desorption mechanism to be operative. We generally applied the gradient that covered the widest range of separation (see Figure 2).

**Dependence of \( R_f \) on molar mass**

The required separation according to chemical composition can most easily be achieved in the absence of any interference caused by molar-mass variations. Recently, we studied the effect of molar mass on the \( R_f \) values. This was achieved by the preparation and separation of copolymers with approximately the same composition \((q_0 = 0.69)\), but varying molar masses. It appeared that the \( R_f \) values are practically independent of molar mass with a possible minor exception in the very low molar-mass region.

In this study we investigated the dependence of \( R_f \) on molar mass in a somewhat more sophisticated way. We carried out the cross-fractionation of an azetropic copolymer of Sty–EMA. This copolymer was obtained from a low-conversion solution process. Then it may be expected that there are no deviations of average composition with molar mass, since the average molar mass is nearly constant during the low-conversion experiment, and the conversion \( CCD \) is negligible as compared with the instantaneous \( CCD \). So, in the absence of molar-mass effects on the separation of Sty–EMA copolymers according to chemical composition, the average composition of each fraction calculated from experimental t.l.c./f.i.d. data is expected to remain constant with increasing fraction number, i.e. decreasing molar mass. The results of the cross-fractionation of the azetropic copolymer are summarized in Table 1. From this table it becomes evident that the average styrene content varies only \( \approx 2\% \) about the mean value, while the molar mass ranges from 15 000 through 2 285 000, which remains within the accuracy of the experimental method.

Complementary to our earlier investigations, the present findings provide conclusive evidence that, under the proper conditions, Sty–EMA copolymers can be separated exclusively according to composition by t.l.c./f.i.d.

**Effect of chemical composition on molar mass**

Our cross-fractionation technique requires fractionation according to molar mass and subsequent analysis of the fractions according to composition. Both separation principles should be as independent as possible. From recent investigations it was shown that the separation of macromolecules according to chemical composition was affected by molar mass to a negligible extent.

However, the first separation carried out by means of s.e.c. is governed by the hydrodynamic volume. In the case of copolymer this hydrodynamic volume may be a function of molar mass as well as composition. Unfortunately, there are no molar-mass standards available for styrene–ethyl methacrylate copolymers. In order to investigate any possible influence of composition on the separation according to hydrodynamic volume, for various (co)polymers, the number-average molar mass was determined by s.e.c. (polystyrene calibration) and osmometry. If there were a strong dependence of composition on hydrodynamic volume, the molar masses as determined by the different methods should differ significantly.

In Table 2 the results are summarized. It appears that, within experimental error, the determination of the molar masses are not significantly affected by variations in composition. So, it is concluded that one single calibration with polystyrene standards may serve as a correct approximation to transform an observed s.e.c. chromatogram to a molar-mass distribution.

**Cross-fractionation**

The characteristics of the copolymers obtained by low-conversion solution processes are mentioned in Table 3. Three samples with average compositions of 35, 52 and 65mol% Sty were analysed by means of cross-fractionation. Since these samples were obtained by low-conversion solution processes, composition drift will be rather small. Hence, it might be expected that the average composition of all molar-mass fractions is equal, and that the composition distributions of each fraction have a symmetric shape.

### Table 1: Effect of molar mass on the average composition of fractions, calculated from the chemical-composition distribution

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Number-average molar mass</th>
<th>Average composition (mol% Sty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>285 000</td>
<td>50.1</td>
</tr>
<tr>
<td>2</td>
<td>123 000</td>
<td>50.9</td>
</tr>
<tr>
<td>3</td>
<td>55 000</td>
<td>49.2</td>
</tr>
<tr>
<td>4</td>
<td>24 000</td>
<td>49.1</td>
</tr>
<tr>
<td>5</td>
<td>15 000</td>
<td>51.1</td>
</tr>
</tbody>
</table>

### Table 2: Molar mass \( (M_n) \) of Sty–EMA (co)polymers experimentally determined by s.e.c. and osmometry

<table>
<thead>
<tr>
<th>( M_n ) (s.e.c.)</th>
<th>( M_n ) (osmometry)</th>
<th>Polymer composition (mol% Sty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 900</td>
<td>10 100</td>
<td>0</td>
</tr>
<tr>
<td>69 000</td>
<td>60 000</td>
<td>20</td>
</tr>
<tr>
<td>48 000</td>
<td>55 000</td>
<td>51</td>
</tr>
<tr>
<td>38 000</td>
<td>71 000</td>
<td>65</td>
</tr>
<tr>
<td>43 000</td>
<td>48 000</td>
<td>100</td>
</tr>
</tbody>
</table>

* Calibration with polystyrene standards

### Table 3: Characteristics of copolymerizations performed till low and high conversion in batch solution processes

<table>
<thead>
<tr>
<th>Initial feed ratio, ( q_0 = [Sty]/[EMA] )</th>
<th>Final mole conversion (%)</th>
<th>Average composition (mol% Sty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-conversion batch solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.67</td>
<td>12</td>
<td>79.8</td>
</tr>
<tr>
<td>2.38</td>
<td>14</td>
<td>64.8</td>
</tr>
<tr>
<td>1.05</td>
<td>14</td>
<td>52.3</td>
</tr>
<tr>
<td>0.34</td>
<td>15</td>
<td>35.1</td>
</tr>
<tr>
<td>0.12</td>
<td>15</td>
<td>19.9</td>
</tr>
<tr>
<td>High-conversion batch solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>69</td>
<td>69.8</td>
</tr>
<tr>
<td>1.12</td>
<td>98</td>
<td>51.7</td>
</tr>
<tr>
<td>0.33</td>
<td>99</td>
<td>26.0</td>
</tr>
</tbody>
</table>
The results of the cross-fractionation are graphically presented in Figures 3a–5a. The same distributions as in Figures 3a–5a are given in Figures 3b–5b, but the point of view has been chosen from the opposite direction. The contours of the experimentally observed and theoretically predicted distributions are given in Figures 3c–5c and 3d–5d, respectively. From a comparison of the observed and predicted contours and taking into account that each sample was divided into only five s.e.c. fractions, it can be inferred that the agreement is good. It appears that the distributions according to composition within the fractions are symmetrical.

The characteristics of the samples obtained from high-conversion batch solution processes are given in Table 3. These samples were also analysed by cross-fractionation. The resulting two-dimensional distributions regarded from the front and back, as well as the contours of the observed and predicted distributions, are presented in Figures 6–8.

As was expected on the grounds of the experimental set-up, no shift of average composition and peak shape are observed for the fractions as the molar mass increases. Furthermore, the distributions obtained under non-azeotropic conditions show significant asymmetric shape. In this case also, the predicted and observed contours are in favourable agreement.

For a copolymer prepared in an emulsion process till very high conversion (98%), striking discrepancies are observed between the predicted (based on solution kinetics) and observed distributions. The shape and the position of the tops of the distribution deviate significantly from that observed in the 'solution samples'. The results are presented in Figure 9. From these results, it might be inferred that, besides the expected polymerization in the bulk of the reaction loci, propagation must also take place at other places within the intrinsically heterogeneous system.

These results emphasize the validity of the cross-fractionation method. Furthermore, these results may provide important information to improve kinetic models describing high-conversion kinetics and may be applied as a powerful tool in understanding relations between polymer structure and physical properties.

**CONCLUSIONS**

The results of the present investigation show that cross-fractionation of Sty-EMA copolymers can be carried out successfully by s.e.c. and subsequent analysis by t.l.c./f.i.d. In s.e.c. analysis, it appeared that the separation of the copolymers according to molar mass is only slightly influenced by the polymer composition; also the separation by t.l.c. appears to be nearly independent of molar mass.

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**Figure 3** (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 20 mol% Sty and obtained by low-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution.
Figure 4  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 52 mol% Sty and obtained by low-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution

Figure 5  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 65 mol% Sty and obtained by low-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution
Figure 6  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 26 mol% Sty and obtained by high-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution.

Figure 7  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 52 mol% Sty and obtained by high-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution.
Figure 8  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 70 mol% Sty and obtained by high-conversion solution process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution. (d) Contours of the predicted distribution.

Figure 9  (a) Experimentally observed two-dimensional distribution according to chemical composition and log molar mass of a copolymer having an average composition of 20 mol% Sty and obtained by high-conversion emulsion process. (b) Same distribution as in (a) but the point of view has been chosen from the opposite direction. (c) Contours of the experimentally observed distribution.
Two-dimensional distributions and contours of these distributions according to molar mass and composition can be obtained from experimental data. Furthermore, a method is proposed to predict the MMCCD of copolymers obtained by high-conversion batch solution processes, if desired. The observed and predicted contours of the distributions are in favourable agreement, proving the validity of the present findings as a key in model studies on relations between copolymerization kinetics and copolymer microstructure.

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