

Determination of Chemical Composition Distribution in a High-Conversion Copolymer of Styrene and Methyl Acrylate by Cross Fractionation

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ABSTRACT: The chemical composition distribution (CCD) of a high-conversion copolymer of styrene and methyl acrylate was determined by cross fractionation and compared with theoretical CCD. Two systems of chloroform–cyclohexane and 2-hydroxyethyl methyl ether–methanol were found to be appropriate for the cross fractionation of the copolymer. It was shown that CCD, determined by cross fractionation, is in fairly good agreement with the value calculated from the classical theory of copolymerization. What is called the gel-effect appears to be negligible in CCD.

KEY WORDS Chemical Composition Distribution / Compositional Fractionation / Cross Fractionation / Styrene–Methyl Acrylate Copolymer / High Conversion /

Copolymers generally have a chemical composition distribution (CCD) as well as a molecular weight distribution (MWD). It is important in the study of a copolymer to determine its CCD. Among several methods proposed for this determination, cross fractionation,^{1–4} thin-layer chromatography,^{5–7} and high-performance liquid chromatography⁸ can give quantitative results. Cross fractionation was suggested in the early 1950's⁹ and has been shown to be the most reliable method available at present. Theoretical calculations² show that CCD obtained by cross fractionation is very close to the actual CCD irrespective of molecular weight. But, one-direction fractionation can give only a CCD narrower than the true one because of the effect of molecular weight. This has been proved experimentally by us³ and also by Stejskal and Kratochvil.⁴ However, only a few cross fractionation experiments have been reported, because of the laborious experimental procedures required. Cross fractionations were thus carried out only for cellulose acetate,⁹ copolymers of *N*-vinylpyrrolidone and vinyl acetate,¹⁰ styrene and butadiene,¹¹ styrene and methyl methacrylate,³ styrene and acrylonitrile,¹² styrene and 2-methoxyethyl methacrylate,⁴ and

partially-substituted poly(methyl methacrylate)¹³

In the present paper, the CCD of a high-conversion random copolymer of styrene (S) and methyl acrylate (MA) was determined by cross fractionation and compared with the theoretical calculation. This copolymer was used in previous work,¹⁴ wherein the MWD and the relationship between point-by-point chemical composition and molecular weight in the sample were found to be affected by the so-called gel-effect. The CCD determined by cross fractionation in the present work was, however, in fairly good agreement with values calculated from the classical theory of copolymerization which does not take the gel-effect into account.

EXPERIMENTAL

Materials

The present work was done with the same whole copolymer of styrene and methyl acrylate used in previous work (B-60).¹⁴ This copolymer was prepared by bulk polymerization from a monomer mixture containing of 60.0 mol%. The conversion was 92.0 wt%. The MA-content of the copolymer

was 56.4 mol% by elemental analysis of carbon and hydrogen* and 56.0 mol% by the ^1H NMR method in a deuteriochloroform solution, using a JNM-MH-60 spectrometer of Japan Electron Optics (Tokyo). The number-average molecular weight was found to be 4.82×10^5 by a Knauer high-speed membrane osmometer (West Germany), using 25°C butanone-2 as solvent. Low-conversion samples of N-45 (MA-content/mol% = 46.6, $M_n \times 10^{-5} = 2.61$), N-60 (57.3, 2.76) and N-75 (77.9, 3.02) were also used to find fractionation systems. The preparation method of the samples was described in detail in our previous paper.¹⁴

Solvents of reagent grade were further purified by the following ways Chloroform was dried with CaCl_2 and distilled fractionally. Cyclohexane was washed with sulfuric acid and water several times, dried with CaCl_2 , and distilled. 2-Hydroxyethyl methyl ether was dried with Na_2CO_3 and distilled under reduced nitrogen atmosphere. Methanol was used following simple distillation.

Searching for Fractionation Systems

To carry out cross fractionation, two fractionation systems were needed. These systems must be different in sign with respect to the fractionation parameter K , which is given for a solvent-nonsolvent system by,¹⁵

$$K = (v_1 - v_1')(\chi_{1,MA} - \chi_{1,S}) + (v_2 - v_2')(\chi_{2,MA} - \chi_{2,S}) \quad (1)$$

v_i and v_i' are the volume fractions of solvent i (1 or 2) in the supernatant and precipitated phases, respectively, and $\chi_{i,MA}$ and $\chi_{i,S}$ are the interaction parameters of solvent i with monomeric units, MA and S, respectively. As solvents for two fractionation systems with positive and negative K , solvents dissolving polystyrene but not dissolving poly(methyl acrylate) or *vice versa* were chosen from published data.¹⁸ Three low-conversion samples (N-45, N-60, and N-75) were dissolved in good solvents such as toluene, ethylbenzene, chloroform etc., and the solutions were titrated by cyclohexane and decalin. Chloroform-cyclohexane system (I) was selected as the system with a positive K , since, among the systems examined, this system exhibited

the greatest dependence of the volume ratio of solvent and precipitant at the cloud point on the MA-content of the sample and a clear phase separation. 2-Hydroxyethyl methyl ether and 2-hydroxyethyl ethyl ether were selected as the solvent for the system with a negative K , respectively. The three copolymer samples were dissolved in these solvents and the solutions were titrated by precipitants such as methanol, ethanol, 2-propanol etc., respectively. On the basis of the criterion mentioned above, 2-hydroxyethyl methyl ether-methanol system (II) was selected as the fractionation system with a negative K .

Fractionation Procedures

One-direction fractionations in systems (I) and (II) were carried out first. In system (I), the sample of 2.485 g was separated into 5 fractions at 25°C by a successive precipitation method. The first fraction was separated at a polymer concentration of 5.67 g dm^{-3} , and the volume ratio of the precipitant (cyclohexane) was 0.795. The equilibration time was one or two days for each fraction. The fractions, separated as precipitated phases, were diluted with chloroform and again precipitated by pouring them into methanol. They were dried *in vacuo* until constant weights were attained.

In system (II), the sample was fractionated into 6 fractions at 25°C by a column elution method. The sample was deposited on glass beads about 170 mesh in size, by slowly evaporating the solvent, tetrahydrofuran. The glass beads coated by the sample were air-dried, then further dried *in vacuo*, and passed through a sieve of 50 mesh. The glass beads were then packed in a glass column 3.6 cm in diameter and 149 cm in height. The sample charged in the column was 3.163 g. Each fraction was eluted with solvent system (II) of about 550 cm^3 , which was almost equal to the hold-up volume of the glass beads column. The flow rate of the eluent was about $5 \text{ cm}^3 \text{ min}^{-1}$. The polymer concentration at which the first fraction was separated was 5.75 g dm^{-3} and the volume fraction of the precipitant (methanol) was 0.359. The volume fraction of the precipitant decreased with fraction number. The equilibration time was about 2–3 h for each fraction. The fractions, eluted as supernatant phases, were concentrated by vacuum evaporation and isolated in the same manner as in one-direction fractionation with system (I).

* The MA-content of the sample (B-60) was reported to be 60.2 mol% in Table III of the previous paper.¹⁴ However, it was a typographical error.

The cross fractionation of the sample was carried out using both systems (I) and (II). First, a 5.058 g sample was fractionated into 4 intermediate fractions. The successive precipitation method was used in the first step, since the amount of sample was comparatively large. According to theory,² for the sample with an L-shaped CCD such as the present sample, fractionation by chemical composition can be expected to be more effective if the sample is precipitated from the tail side to the peak side of the CCD. Therefore, system (I) precipitation of the components with higher MA-content (the tail side) was used in the fractionation. The respective intermediate fractions were separated into 4 or 5 fractions in System (II). The column elution method was applied, since the fractionation had to be carried out 4 times. The total number of final fractions was 19. The fractionation procedure was the same as that for one-direction fractionations. The MA-content of each fraction was determined by elemental analysis of carbon and hydrogen.

RESULTS

Experimental data obtained by one-direction fractionations in system (I) and (II) and by cross fractionation are shown in Tables I, II, and III, respectively. The amount of sample recovered for each fractionation was close to that for each charged sample, as shown in tables. The average MA-content calculated from the fractionation data is in good agreement with original sample values in all cases.

The CCD curves obtained by one-direction fractionation in the respective systems are illus-

Table I. Results of one-direction fractionation in system (I)^a

Fraction No.	Weight fraction	MA-content/mol%
1	0.237	74.0
2	0.150	60.8
3	0.456	50.2
4	0.130	46.4
5	0.027	46.9
Average		56.8

^a Sample recovery was 0.980.

trated in Figure 1. The CCD curve obtained from the data of cross fractionation is shown in Figure 2. The curves in Figure 1 were constructed by plotting the data of Tables I and II in the order of fractionation steps, while the curve in Figure 2 was

Table II. Results of one-direction fractionation in system (II)^a

Fraction No.	Weight fraction	MA-content/mol%
1	0.036	72.2
2	0.112	69.7
3	0.144	62.7
4	0.289	56.7
5	0.244	51.8
6	0.175	46.7
Average		56.6

^a Sample recovery was 0.965.

Table III. Results of cross fractionation^a

Fraction No.	Weight fraction	MA-content/mol%
1-1	0.0338	86.0
1-2	0.0290	76.6
1-3	0.0298	63.0
1-4	0.0351	59.0
2-1	0.0492	69.8
2-2	0.0168	67.6
2-3	0.0979	63.2
2-4	0.1017	57.0
2-5	0.0318	47.3
3-1	0.0700	54.5
3-2	0.1063	51.9
3-3	0.1069	49.8
3-4	0.1768	48.8
3-5	0.0403	46.4
4-1	0.0248	62.0
4-2	0.0115	47.4
4-3	0.0121	45.9
4-4	0.0186	45.6
4-5	0.0076	44.4
Average		56.1

^a Sample recovery was 0.943.

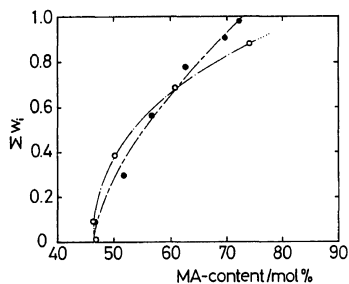


Figure 1. The integral CCD curves obtained by one-direction fractionations: —○—, system (I); —●—, system (II).

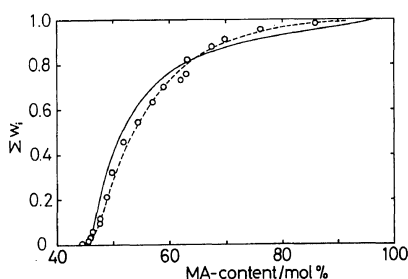


Figure 2. The integral CCD curves obtained by cross fractionation and theoretical calculation: --○--, experimental curve; —, theoretical curve.

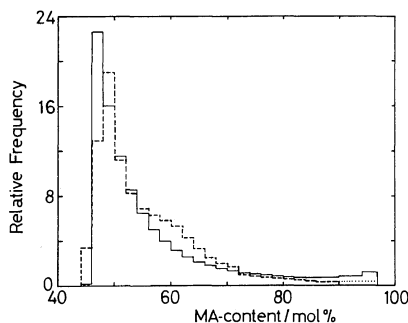


Figure 3. The differential CCD curves obtained by experiment (dashed line) and theoretical calculation (solid line).

constructed by rearranging the data of Table III in order of increasing MA-content. The differential CCD curve from cross fractionation was calculated by differentiating the dashed line fitting the data points, and is illustrated in Figure 3. The curve shows the L-shaped feature, which is typical of CCD of high-conversion copolymers prepared in batch.

DISCUSSION

For comparison with the experimentally determined CCD curve, the theoretical CCD due to the drift of monomer composition with conversion was calculated by the equations of Mayer and Lowry.¹⁶ The mole-conversion in these equations was changed to weight-conversion, since the CCD obtained by experiment is expressed in terms of weight fractions of the respective components. Thus, the following equations were derived for the integral distribution function,

$$1 - \frac{w}{w^0} = 1 - \left(\frac{f_1}{f_1^0} \right)^\alpha \left(\frac{1-f_1}{1-f_1^0} \right)^\beta \left(\frac{f_1^0 - \delta}{f_1 - \delta} \right)^\gamma \times \frac{[(M_1 - M_2)f_1 + M_2]}{[(M_1 - M_2)f_1^0 + M_2]} \quad (2)$$

and for the differential distribution function

$$\frac{1}{w^0} \frac{dw}{dF_1} = \left(\frac{f_1}{f_1^0} \right)^\alpha \left(\frac{1-f_1}{1-f_1^0} \right)^\beta \left(\frac{f_1^0 - \delta}{f_1 - \delta} \right)^\gamma \times \left(\frac{\alpha}{f_1} - \frac{\beta}{1-f_1} - \frac{\gamma}{f_1 - \delta} \right) \frac{[(M_1 - M_2)f_1 + M_1]}{[(M_1 - M_2)f_1 + M_2]} \times \frac{[(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2]^2}{[(r_1 + r_2 - 2r_1r_2)f_1^2 + 2r_2(r_1 - 1)f_1 + r_2]} \quad (3)$$

where $1 - (w/w^0)$ is the weight conversion at the monomer composition f_1 (mole fraction of monomer-1), F_1 is the composition of the copolymer instantaneously obtained from the monomer mixture of f_1 ; r_1 and r_2 are the monomer-reactivity ratios of the respective monomers, M_1 and M_2 are the molecular weights of the monomeric units, respectively, $\alpha = r_2/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, $\gamma = (1 - r_1 - r_2)/(1 - r_1)(1 - r_2)$ and $\delta = (1 - r_2)/(2 - r_1 - r_2)$. The superscript zero indicates initial values. F_1 , $(1 - w/w^0)$ and $(1/w^0)(dw/dF_1)$ were calculated as functions of f_1 , using eq 2 and 3. The gel-effect was not taken into account in this calculation. The actual calculation was carried out with $M_1 = 86.09$, $M_2 = 104.15$, $r_1 = 0.18$, $r_2 = 0.75$,¹⁷ (MA is denoted by 1) and the initial monomer composition and weight-conversion shown in the EXPERIMENTAL section.

The integral and differential CCD curves thus calculated are shown in Figures 2 and 3, respectively, along with the experimental curves

obtained by cross fractionation. These figures show a fairly good agreement between the calculated and experimental curves. Since the gel-effect was not taken into account in this calculation, it may be concluded that the gel-effect on CCD, if any, is not as serious as that on MWD.

Strictly speaking, the MA-content of the two fractions (No. 4-4 and 4-5) are slightly outside the theoretical lower limit (45.9 mol%). That is, a short tail is found on the left side of the peak in Figures 2 and 3. It is known theoretically²⁰ and was confirmed experimentally³ that instantaneous copolymers have the so-called statistical composition heterogeneity. The tail on the lower MA-content side of the CCD curve may be due to this statistical fluctuation in chemical composition.

As is clear by a comparison of Figures 1 and 2, the CCD curve obtained by cross fractionation is broader than those obtained by one-direction fractionation. This fact is in agreement with the experimental results of our previous work¹¹ and the results of Stejskal and Kratochvíl,⁴ and also with a theoretical prediction.² Since this difference stems from the principles of the two methods, there is probably no possibility of reversing such a situation even if the number of fractions in the one-direction fractionation (4 or 5, see Tables I and II) were increased to that in the cross fractionation (19, see Table III).

Comparing the results from one-direction fractionations in Figure 1, we found the CCD obtained in system (I) to be broader than that in system (II). This shows that the absolute value of K may be larger in system (I) than in system (II), since the column elution method was found to be more effective than the successive precipitation method in compositional fractionation when using the same fractionation system.¹⁹

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