# Study of the Distribution of Chemical Composition in Low-Conversion Copolymer by Cross-Fractionation

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ABSTRACT: Styrene and methyl methacrylate were copolymerized at a mixture composition close to the azeotropic point. The copolymerization was terminated at relatively low conversion. This copolymer sample was fractionated by a cross-fractionation method using systems of both acetone–acetonitrile and *n*-butyl chloride–cyclohexane. The chemical composition and molecular weight distribution curves were constructed from the fractionation data. Both distribution curves agreed with curves calculated from the theory of Stockmayer on the assumption that the termination occurs by coupling only. It is concluded that Stockmayer's theory is in satisfactory agreement with experimental results, that combination appears to be predominant in copolymerization of styrene and methyl methacrylate, and that the cross-fractionation method can give reliable chemical composition and molecular weight distributions.

Several authors[1–3] have derived a differential equation relating the overall chemical composition of a copolymer to that of the parent monomer mixture. The agreement between this equation and experimental data has been extensively demonstrated. Integration of this equation has been carried out to calculate the chemical composition distribution curves of high-conversion copolymers.[4–6] The differential distribution curve of chemical composition thus obtained shows either an L shape with a single peak and a tail or a U shape indicating a cleavage of compositions into two different groups.[4] Some experimental results[7–10] were shown to agree, at least qualitatively, with curves calculated from the equation. In such calculations of chemical composition distributions, it is assumed that only a copolymer of uniform composition is obtained from a monomer mixture at a certain composition.

On the other hand, since the polymerization degree of a copolymer is finite, the chemical compositions of individual molecules cannot be identical. That is, even in the copolymer formed during a differential time interval, there must exist a chemical composition distribution. A theory concerning this problem was formulated by Simha and Branson,[11] and then the chemical composition and chain length distributions of a copolymer formed during a differential time interval were given in simple and tractable forms by Stockmayer.[12] According to his theory, the chemical composition distribution of a copolymer formed during a differential time interval is Gaussian. In contrast to speculations based on the theory of Skeist and others,[4–6] therefore, the distribution curve of a high-conversion copolymer may have a short tail on the opposite side in addition to the main tail formed during the polymerization process. However, no experimental test of this speculation has been published, except for a styrene–butadiene copolymer reported elsewhere,[13] since experimental methods to detect the existence of a short tail in a distribution curve have been unknown.

It is the purpose of this paper to examine the theory of Stockmayer by determining the chemical composition and chain length distributions of a low-conversion copolymer prepared under well-defined experimental conditions, by means of a cross-fractionation method.

## Experimental Section

**Copolymer Sample.** Since equal weights were assigned for simplicity to the two species of monomer unit in Stockmayer's equations, it is convenient to use a copolymer for which the molecular weights of the two species of monomer unit are close to one another. Moreover, the properties of the monomer species should be as different as possible with respect to interaction with the solvents used in fractionation. Taking into account these requirements, a styrene–methyl methacrylate copolymer was selected as the sample in the present work.

The sample copolymer was made by bulk polymerization at 60° under nitrogen atmosphere, using benzoyl peroxide as the initiator. The mole fraction of methyl methacrylate in the monomer mixture was 0.509 which is close to the azeotropic composition. The polymerization was terminated at 14% conversion. This sample can be regarded as a copolymer formed during a differential time interval assured in the theory of Stockmayer. Purification of the sample was carried out by precipitating the sample from dioxane with methanol.

The number average molecular weight of the sample was $21.3 \times 10^4$, which was determined with a Hewlett–Packard 502 high-speed membrane osmometer in toluene at 25.0°. The mole fraction of methyl methacrylate in the sample was

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TABLE I

| Fraction no. | Weight fraction | $M_n \times 10^{-4}$ | MMA content, mol % |
|---|---|---|---|
| 1-1 | 0.0253 | 38.3 | 52.9 |
| 1-2 | 0.0349 | 41.5 | 50.8 |
| 1-3 | 0.0206 | 50.6 | 50.2 |
| 1-4 | 0.0368 | 21.3 | 49.1 |
| 2-1 | 0.0194 | 60.2 | 50.1 |
| 2-2 | 0.0198 | 84.3 | 48.2 |
| 2-3 | 0.0177 | 79.1 | 47.1 |
| 2-4 | 0.0161 | 14.7 | 48.8 |
| 3-1 | 0.0275 | 74.4 | 52.8 |
| 3-2 | 0.0338 | 87.2 | 47.8 |
| 3-3 | 0.0303 | 43.6 | 48.4 |
| 3-4 | 0.0245 | 42.9 | 48.9 |
| 3-5 | 0.0408 | 25.3 | 48.6 |
| 4-1 | 0.0240 | 50.6 | 49.7 |
| 4-2 | 0.0295 | 47.7 | 49.2 |
| 4-3 | 0.0344 | 39.5 | 50.2 |
| 4-4 | 0.0300 | 35.6 | 49.4 |
| 4-5 | 0.0281 | 31.2 | 49.7 |
| 4-6 | 0.0225 | 26.4 | 46.7 |
| 4-7 | 0.0151 | 11.7 | 48.9 |
| 5-1 | 0.0166 | 32.0 | 49.8 |
| 5-2 | 0.0207 | 35.1 | 50.7 |
| 5-3 | 0.0525 | 33.3 | 48.9 |
| 5-4 | 0.0504 | 31.2 | 49.6 |
| 5-5 | 0.0357 | 23.4 | 49.7 |
| 5-6 | 0.0270 | 20.6 | 49.7 |
| 5-7 | 0.0257 | 14.1 | 50.9 |
| 6-1 | 0.0201 | 20.2 | 53.5 |
| 6-2 | 0.0247 | 19.2 | 51.6 |
| 6-3 | 0.0282 | 16.4 | 50.4 |
| 6-4 | 0.0322 | 14.1 | 49.5 |
| 6-5 | 0.0310 | 13.1 | 49.1 |
| 6-6 | 0.0263 | 11.2 | 48.7 |
| 6-7 | 0.0250 | 9.4 | 49.0 |
| 6-8 | 0.0528 | 4.9 | 50.0 |
|  |  | Av 20.7 | 49.7 |

0.495, which was determined by an nmr method[14–16] with a JNM-MH-60 spectrometer of Japan Electron Optics.

Purification of the styrene and methyl methacrylate monomers used in the copolymerization was carried out by distillation under nitrogen atmosphere at reduced pressures of 50–90 mm, respectively.

**Fractionation Procedure.** In order to carry out cross-fractionation, it is necessary to find two different solvent–nonsolvent mixtures in which the interaction parameter of monomer A, $\chi_A$, is larger than that of monomer B, $\chi_B$, and *vice versa*.[13,17] Quite a number of solvent–nonsolvent systems were tested. The volume ratios of solvent–nonsolvent to cause the first phase separation of two copolymer samples different from one another in chemical composition were compared, and then the systems which showed the greatest difference in volume ratios for the two samples were selected. Thus, the acetone–acetonitrile system (I) and the *n*-butyl chloride–cyclohexane system (II) were found to be appropriate for the present purpose.

Purification of acetone was carried out by drying first-grade reagent with $CaSO_4$ followed by fractional distillation.

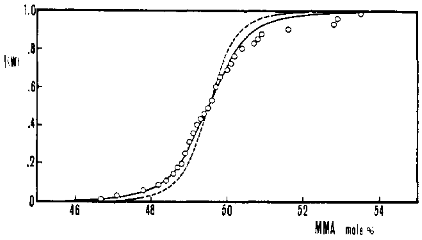

Figure 1. Integral chemical composition distribution curves: ○, experimental data; ——, calculated for the case of termination by coupling; – – –, calculated for the case of termination by disproportionation.

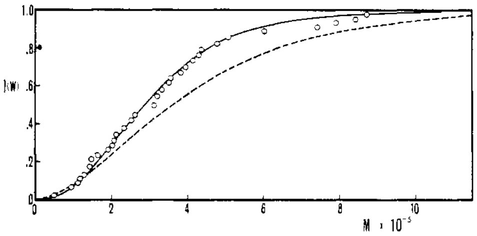

Figure 2. Integral molecular weight distribution curves: ○, experimental data; ——, calculated for the case of termination by coupling; – – –, calculated for the case of termination by disproportionation.

First-grade acetonitrile was purified by drying with $K_2CO_3$ and $Na_2SO_4$ and then by distillation. *n*-Butyl chloride was purified by shaking with concentrated $H_2SO_4$, drying over $CaCl_2$, and then distilling. Practical-grade cyclohexane was passed through silica gel to remove aromatic impurities and then fractionally distilled over sodium wire.

In the cross-fractionation, about 15 g of the copolymer sample was divided into six intermediate fractions by successive precipitations in system I, and then each intermediate fraction was subdivided into several fractions in system II. Thus, 35 fractions were obtained. Each fractionation was carried out at 25.0 ± 0.01°. The equilibration times were from one to a few days. The polymer concentration at which the first fraction separated was about 0.95 g/100 ml in system I, and from 0.15 to 0.31 g/100 ml in system II. Each fraction thus obtained was precipitated and washed with methanol. Then, the fractions were freeze-dried from dioxane solutions, followed by evacuation for about 24 hr at 40°. The recovery of the sample was 97.1%. Characterization of each fraction was carried out in the same manner as that of the original sample.

## Results

Experimental results of cross-fractionation are shown in Table I. The average chemical composition and molecular weight calculated from the fractionation data agree with the values for the original sample within experimental error. The average values were calculated by

$$\bar{M}_n = 1/\sum_i (w_i/M_{ni}) \qquad (1)$$

$$\bar{\alpha} = \sum_i \alpha_i w_i \qquad (2)$$

The distribution curves of chemical composition and molecular weight calculated from the fractionation data are shown in Figures 1 and 2, respectively, together with theoretical curves as explained below. These curves were obtained by rearranging the data of Table I in

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order of increasing magnitudes (composition or molecular weight).

## Discussion

The chemical composition distribution curve obtained from the experimental data extends around the average chemical composition of the original sample. Several pairs of reactivity ratios in the copolymerization of styrene and methyl methacrylate have been reported.[18-21] Using these values, the expected width of the chemical composition distribution caused by a drift of monomer mixture composition was calculated by Meyer and Lowry's equation[6] and found to be 0.26 mol % at most. In the present method of chemical composition distribution determination, experimental errors also produce an apparent distribution in the chemical composition of the sample, even if the sample has a uniform composition. We estimate the effect of such experimental errors on the width of the distribution as about 1.5 mol % at most. The chemical composition distribution curve obtained from the experimental data is clearly too broad to be attributed only to these experimental errors. Therefore, we conclude that the present experimental results support the statement that the copolymer formed during a differential time interval has a chemical composition distribution.

According to Stockmayer,[12] the distributions of chain length and chemical composition of copolymer radicals formed during a differential time interval are expressed by a compact equation (3) where $y = p - p_0 = q_0 - q$

$$w(l, y)\mathrm{d}l\mathrm{d}y = [\exp(-l/\lambda)l\mathrm{d}l/\lambda^2][(l/2\pi p_0q_0\kappa)^{1/2} \times \exp(-ly^2/2p_0q_0\kappa)\mathrm{d}y] \quad (3)$$

$\kappa = [1 - 4p_0q_0(1 - r_1r_2)]^{1/2}$, $l$ is the polymerization degree of an individual copolymer radical, $\lambda$ is the number average chain length (polymerization degree) of the overall copolymer radicals, $r_1$ and $r_2$ are the monomer reactivity ratios, $p = 1 - q$ is the chemical composition of an individual chain expressed in mole fraction of component 1, and $p_0 = 1 - q_0$ is the overall chemical composition. In this equation, equal weights of two types of monomer unit are assumed. If the copolymerization were terminated entirely by disproportionation, eq 3 would also give the distribution of the stable copolymer obtained. In case a fraction $\rho$ of the chain radicals is terminated by combination, the distribution of the stable copolymer would be

$$w(l, y)\mathrm{d}l\mathrm{d}y = [\exp(-l/\lambda)(1 - \rho + \rho l/2\lambda)l\mathrm{d}l/\lambda^2] \times [(l/2\pi p_0q_0\kappa)^{1/2} \exp(-ly^2/2p_0q_0\kappa)\mathrm{d}y] \quad (4)$$

where $\lambda$ still is the number average length of the radicals. The termination process affects the distribution of chain length only. The chain length distribution irrespective of chemical composition is found in the following forms respectively by integrating eq 3 and 4 over $y$

$$w(l)\mathrm{d}l = \exp(-l/\lambda)l\mathrm{d}l/\lambda^2 \quad (5)$$

or

$$w(l)\mathrm{d}l = \exp(-l/\lambda)(1 - \rho + \rho l/2\lambda)l\mathrm{d}l/\lambda^2 \quad (6)$$

The chemical composition distribution irrespective of chain length is found by integrating eq 3 over $l$. The result is given by

$$w(y)\mathrm{d}y = 3dz/4(1 + z^2)^{5/2} \quad (7)$$

where

$$z^2 = \lambda y^2/2p_0q_0\kappa$$

The distribution curves were calculated from eq 5, 6, and 7 using the following constants: both $r_1$ and $r_2$ are 0.50,[2] $p_0 = 0.495$, $q_0 = 0.505$. Although $\lambda$ may still change with conversion even at the azeotropic composition, $\lambda$ is assumed to be constant in the course of the polymerization because of the relatively low conversion. That is, $\lambda = 2090$ when $\rho = 0$ and $\lambda = 1045$ in the case of $\rho = 1$, in order to give the number average polymerization degree of the original sample. The calculations were carried out for the two extreme cases in which the termination occurs by disproportionation only and by combination only. The practical polymerization would be between these two extreme cases. In both Figures 1 and 2, the dashed line expresses the former case while the solid line expresses the latter case.

Both distribution curves of chemical composition and chain length constructed from the experimental data show satisfactory agreement with the calculated ones. It can be concluded that the copolymerization equations of Stockmayer are valid. Figures 1 and 2, moreover, appear to show that the termination in the copolymerization of styrene and methyl methacrylate occurs due to combination. Taking into account the accuracy of our chemical composition determination and, moreover, the fact that fractionation schemes tend to underestimate the breadth of a molecular weight distribution, however, the comparisons between theory and experiments shown in Figures 1 and 2 are not strict enough to conclude that termination occurs *only* due to combination and that disproportionation is negligible. Therefore, we would like to note only that this result is consistent with the work of Bevington, Melville, and Taylor,[22] who showed by using an initiator labeled with $^{14}$C that the disproportionation of radicals is negligible in the copolymerization of this system at 60°.

Thus, we may conclude that (1) the theory of Stockmayer is in satisfactory agreement with experimental results, (2) combination appears to be predominant in the copolymerization of styrene and methyl methacrylate, and (3) cross-fractionation can give reliable chemical composition and molecular weight distributions.

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