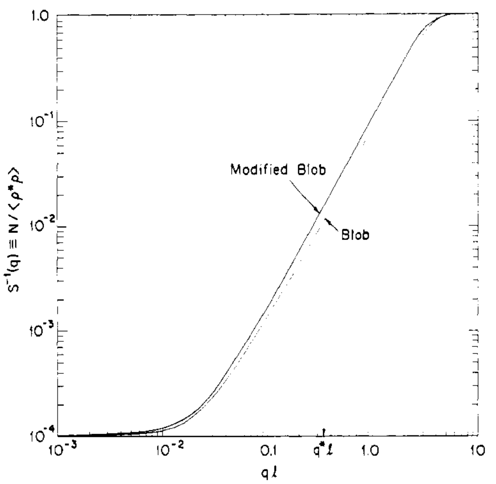

Figure 5. Comparison of the original and modified blob hypotheses in the case of the inverse static form factor $S^{-1}(q)$ as a function of q.

$\sim q^{-2}$ for $q > q^*$, which was reported by Farnoux et al.[10] using the original blob model, is even less apparent in the case of modified blob model.

Conclusion

The present modification of the blob hypothesis improves the numerical accuracy of the model in the region where $N/N_\tau \sim 1$, where discrepancies with experiment may be as large as 15%, as reported in ref 1. This improvement is obtained by abandoning the existence of only two discrete exponents in the swelling of sections of a chain, as postulated in the original blob model, but retaining the more fundamental idea that the smaller sections swell less than the longer ones. Therefore, all the qualitative predictions of the original blob concept remain valid. A recent work by Francois[11] also describes a procedure for improving the original blob model in the same direction as above.

The blob concept, in its modified or original form, provides a workable model for the equilibrium distribution $\psi_0(\mathbf{R}_{ij})$ for the vector distance between two monomers and enables one to calculate consistently several single-chain properties like the first cumulant $\Omega(q)$, α_H, α_s, and $S(q)$ as functions of q, molecular weight, and temperature, with one adjustable parameter. As such, its predictions can be tested by a variety of experiments over large ranges of experimental conditions, as we demonstrated in ref 1.

Acknowledgment. Fruitful discussions with Professor G. C. Summerfield are acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

References and Notes

(1) Akcasu, Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(2) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2462.
(3) Daoud, M. Thesis, Université de Paris VI, 1977.
(4) Benmouna, M.; Akcasu, Z. *Macromolecules* **1978**, *11*, 1187.
(5) Han, C. C. *Polymer* **1979**, *20*, 1083.
(6) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(7) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(8) Fujita, H.; Norisuye, T. *J. Chem. Phys.* **1970**, *52*, 1115.
(9) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 3123.
(10) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Paris)* **1978**, *39*, 77.
(11) Francois, J.; Schwartz, T.; Weill, G. *Macromolecules* **1980**, *13*, 564.

Study of the Statistical Chemical Heterogeneity of Copolymers by Cross-Fractionation

Jaroslav Stejskal,* Pavel Kratochvíl, and Dagmar Straková

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received March 31, 1980*

ABSTRACT: The distribution functions of chemical composition describing the statistical heterogeneity of copolymers are discussed. The distribution functions for termination by disproportionation and combination are similar. Theoretical prediction is compared with the experimental result of cross-fractionation of an azeotropic copolymer of styrene and 2-methoxyethyl methacrylate. The experimental distribution function is much narrower than the predicted one, which suggests the limited efficiency of cross-fractionation.

Unlike the comparatively well-described[1-3] conversion chemical heterogeneity of statistical copolymers, the so-called statistical chemical heterogeneity of these copolymers has so far attracted less attention. This is justified in many respects because as a rule such a type of chemical heterogeneity is of a much smaller extent. Cases may be found, however, especially with low molecular weight copolymers, where statistical heterogeneity is not negligible[4] and may affect the experimental characterization of these copolymers, e.g., by light scattering. The importance of an analysis of statistical heterogeneity has lately increased owing to the development of novel and more sensitive methods of determination of the distribution of chemical composition (cross-fractionation,[5,6] adsorption high-speed liquid chromatography,[7,8] etc.).

The cross-fractionation of copolymers dealt with in this paper consists of a twofold fractionation in different solvent systems. Primary fractions obtained by fractionation in a system where chains richer in one type of monomeric unit are preferentially precipitated are refractionated in another solvent system in which, on the contrary, macromolecules with a higher content of the other type of monomeric unit are preferentially separated. This procedure seems to be one of the most efficient methods of copolymer fractionation by chemical composition. For this reason, cross-fractionation was used in the present study of comparatively small differences in chemical composition of copolymer molecules, given by the statistical nature of copolymer chain formation.

The theoretical analysis of the statistical heterogeneity is offered in a fundamental paper by Stockmayer[9] for the case of equal molecular weights of both types of monomeric units. The two-dimensional differential weight distribution of chemical composition has been derived and expressed

0024-9297/81/2214-0150$01.00/0 © 1981 American Chemical Society

in terms of deviations, y, in the composition of the individual copolymer chains, w, from the mean composition, $\bar{w}$ (i.e., $y = w - \bar{w}$), and of the degrees of polymerization, P, in the form

$$f(P,y) = \left(1 - \rho + \frac{\rho P}{2P_n^*}\right)\frac{P}{P_n^{*2}} \times \exp\left(-\frac{P}{P_n^*}\right)\left(\frac{P}{2\pi\bar{w}(1-\bar{w})k}\right)^{1/2} \exp\left(-\frac{Py^2}{2\bar{w}(1-\bar{w})k}\right) \quad (1)$$

Here, compositions are given by the weight or mole fraction of one type of monomeric unit in the copolymer, the two fractions being equal with the above assumption. ρ is the number fraction of radicals with the degree of polymerization P_n^* terminated by recombination ($\rho = 0$ for termination exclusively by disproportionation); for the number-average degree of polymerization of the copolymer, it follows that $P_n = P_n^*/(1 - \rho/2)$. Finally

$$k = [1 - 4\bar{w}(1-\bar{w})(1 - r_1r_2)]^{1/2} \quad (2)$$

where r_1 and r_2 are the copolymerization parameters. A generalization of eq 1 comprising different molecular weights of monomers meets with difficulties of mathematical character.

By integrating eq 1 over all deviations y, one obtains the marginal distribution function of the degrees of polymerization, analogous to the distribution functions for homopolymers.[9]

Similarly, integration over all degrees of polymerization yields the marginal distribution functions of chemical composition (or its deviations), $g(y)$. For the termination by disproportionation, Stockmayer gives the differential weight distribution function of chemical composition in the form[9]

$$[g_D(y)]\mathrm{d}y = \left[\frac{3}{4(1+z^2)^{5/2}}\right]\mathrm{d}z \quad (3)$$

where

$$z^2 = \frac{P_n^*y^2}{2\bar{w}(1-\bar{w})k} \quad (4)$$

(Here and below, subscripts D and R are used if the quantity is related to the termination exclusively by disproportionation or recombination.)

As the above distribution function is sometimes used not quite rigorously also for termination by recombination, we would like to add a few comments. The derivation of an analogous distribution function for termination by recombination may be useful because this very way of termination seems to prevail in real polymerizations. Similarly to Teramachi et al.,[6] we shall compare the experimental results obtained from cross-fractionation with theoretical prediction.

Theoretical Section

By integration of the Stockmayer distribution function (1) over all the degrees of polymerization P, the marginal distribution function of deviations of chemical composition y is obtained in the form

$$g(y) = \frac{3}{4}(1-\rho)\frac{\Xi}{(1+z^2)^{5/2}} + \frac{15}{16}\rho\frac{\Xi}{(1+z^2)^{7/2}} \quad (5)$$

where

$$\Xi = \left(\frac{P_n^*}{2\bar{w}(1-\bar{w})k}\right)^{1/2} \quad (6)$$

$$z^2 = \Xi^2y^2$$

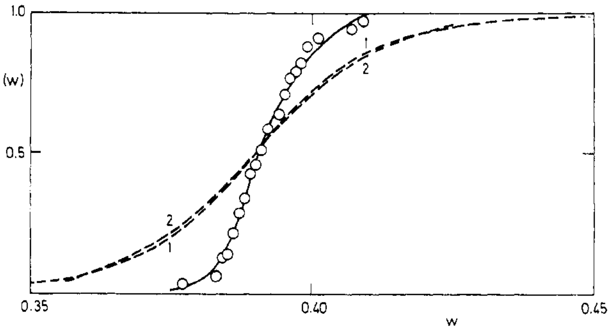

Figure 1. Integral weight distribution function $G(w)$ of chemical composition w, given by the weight fraction of styrene units, for an azeotropic copolymer of styrene and 2-methoxyethyl methacrylate: (—) experimental result of cross-fractionation; (- - -) calculated distribution functions for termination by disproportionation (1) and combination (2). These functions have been calculated by integrating the respective differential functions (7) and (8).

(cf. Appendix). Essentially the same result has recently been arrived at by Kuchanov.[10] For the termination by disproportionation ($\rho = 0$, $P_n = P_n^*$), we obtain the distribution function

$$g_D(y) = \frac{3\Xi}{4(1+z^2)^{5/2}} \quad (7)$$

identical with Stockmayer's distribution function (3). Similarly, for the termination by combination ($\rho = 1$, $P_n = 2P_n^*$), it follows

$$g_R(y) = \frac{15\Xi}{16(1+z^2)^{7/2}} \quad (8)$$

If one wants to characterize quantitatively the distribution width of chemical composition and hence also the statistical heterogeneity, it is expedient to derive the expression for the variance of chemical composition, σ^2 (cf. Appendix)

$$\sigma^2 = \left(1 - \frac{\rho}{2}\right)\frac{\bar{w}(1-\bar{w})k}{P_n^*} \quad (9)$$

For the copolymer with the degree of polymerization P_n the same value results

$$\sigma^2 = \frac{\bar{w}(1-\bar{w})k}{P_n} \quad (10)$$

irrespective of the termination mechanism.

Both distribution functions (7) and (8) for the termination by disproportionation and combination are formally different. Since they have the same position and, according to (10), also the same width, their shape at the same values of the other parameters is very similar (cf. Figure 1).

Experimental Section

The azeotropic copolymer of styrene ($r_S = 0.40$) and 2-methoxyethyl methacrylate[11] ($r_{\mathrm{MEMA}} = 0.46$) was prepared by radical copolymerization in 80 vol % benzene at 60 °C to 8.2 wt % conversion. The initiator, azobis(isobutyronitrile), was twice recrystallized from methanol; the monomers were purified by distillation on laboratory columns. The molecular weight of the copolymer determined by light scattering in toluene was $M_w = 43\,000$; that determined by osmometry, also in toluene, was $M_n = 28\,000$. The ratio $M_w/M_n \doteq 1.5$ suggests termination by combination of polymer radicals. The copolymer composition determined by elemental analysis was 39.4 wt % of styrene.

The copolymer thus prepared was separated by precipitation fractionation in the system benzene–cyclohexane into a series of primary fractions; these were refractionated in the system butanone–methanol. The solvent system for cross-fractionation was chosen on the basis of preliminary fractionation studies as the

Table I
Results of the Cross-Fractionation of an Azeotropic Copolymer of Styrene and 2-Methoxyethyl Methacrylate[a]

n	W_n	w_n	n	W_n	w_n
I-1	0.0147	0.331	IV-1	0.0171	0.399
I-2	0.0111	0.386	IV-2	0.0325	0.398
I-3	0.0212	0.377	IV-3	0.0372	0.394
II-1	0.0755	0.395	IV-4	0.0059	0.385
II-2	0.0496	0.392	IV-5	0.0273	0.383
II-3	0.0500	0.391	V-1	0.0179	0.397
II-4	0.0575	0.388	V-2	0.0434	0.399
II-5	0.0764	0.386	V-3	0.0234	0.401
III-1	0.0488	0.389	V-4	0.0132	0.394
III-2	0.0346	0.390	V-5	0.0641	0.387
III-3	0.0251	0.392	VI-1	0.0299	0.409
III-4	0.0364	0.389	VI-2	0.0275	0.410
III-5	0.0651	0.384	VI-3	0.0374	0.407
			VI-4	0.0572	0.396

[a] W_n is the weight fraction of nth fraction and w_n is its chemical composition given by the weight fraction of styrene. Roman numerals correspond to primary fractions obtained by fractionation in the system benzene–cyclohexane; Arabic numerals denote secondary fractions obtained from the system butanone–methanol.

relatively most efficient one.[12] The fractions were isolated by a standard procedure and weighed, and their composition was determined by elemental analysis (with an error less than 1 wt % styrene). The recovery of the copolymer was 98 wt %.

Results and Discussion

A comparison of the results of the cross-fractionation of an azeotropic copolymer of styrene and 2-methoxyethyl methacrylate (Table I, Figure 1) with the calculated integral distribution functions of chemical composition shows that the experimental distribution function of chemical composition is much narrower than the theoretically predicted one (cf. also the values of variance of chemical composition in Table II). This finding may be explained in different ways. If it is assumed that the fractionated copolymer exhibits chemical heterogeneity predicted by theory, then the most likely cause seems to rest in the limited efficiency of the fractionation by chemical composition. The low efficiency may be either of fundamental character or due to an inappropriate choice of the solvent systems in which cross-fractionation takes place. The solvent systems used in this work have been tested earlier.[12] The copolymers of styrene and 2-methoxyethyl methacrylate with a wide model distribution of chemical composition are separated in this system, with the relatively best efficiency, with respect to chemical composition. It seems, therefore, that even though the cross-fractionation is one of the most efficient methods available nowadays for the separation of copolymers by chemical composition, its separation efficiency is not sufficient for narrow distributions.

The primary fractions differ little in their composition. Their composition given by the weight fraction of styrene is as follows for the individual fractions: I, 0.365; II, 0.390; III, 0.388; IV, 0.393; V, 0.394; VI, 0.404. Here, it is possible to trace out an unpronounced dependence between the composition of a fraction and its ordinal number. For secondary fractions (Table I), which differ still less in composition, such a correlation cannot be detected (cf. also ref 6) because differences in the chemical composition of fractions are comparable, in most cases, with the experimental error in the analytical determination of chemical composition.

It should be pointed out that the normally distributed experimental error in the determination of the chemical composition of fractions would yield a fictitious distribution of chemical composition, similar to the experimental distribution in Figure 1, even with a perfectly homogeneous copolymer. The experimental error in the determination of the composition of our fractions does not account for the width of the observed distribution; it has to be admitted, however, that the distribution function may have been incorrectly broadened due to the experimental error of the analytical method.

Table II
Chemical Composition $\overline{w}$ Given by the Weight Fraction of Styrene, Molecular Weight M_n, and Variance of Chemical Composition σ^2 of Copolymers Used in Cross-Fractionation

copolymer	$\overline{w}$	$10^{-3}M_n$	$10^4\sigma^2$ expt[a]	$10^4\sigma^2$ theor using eq 10
styrene-2-methoxyethyl methacrylate	0.392	28	1.07	4.9
styrene-methyl methacrylate[b]	0.493	213	1.77	0.6

[a] Calculated with the equation $\sigma^2 = \Sigma_n(w_n - \overline{w})^2 W_n$.
[b] Taken from ref 6.

The distribution functions described in the theoretical section have been derived for equal molecular weights of monomeric units. This assumption is not quite fulfilled for the pair styrene–2-methoxyethyl methacrylate, the ratio of molecular weights of monomers being 0.722. For this reason, too, the discussion of experimental data is of a rather qualitative nature.

Teramachi et al.[6] carried out a similar fractionation study with an azeotropic copolymer of styrene and methyl methacrylate. This copolymer is better suited for the comparison between the calculated and experimental distributions because the ratio of molecular weights of monomeric units is almost unity (0.962); the molecular weight of the copolymer was relatively high, however, and consequently (cf. eq 10), the expected statistical heterogeneity was very low (Table II). The above authors found agreement between experimental results and the calculated distribution of chemical composition. Instead of the distribution function of chemical composition for the termination by combination, which for copolymers of styrene and methyl methacrylate is the only way of termination,[13] the distribution function for disproportionation has been used, with half the value of the degree of polymerization substituted into it. In our opinion, this leads to a fictitious broadening of the calculated distribution of chemical composition. Parenthetically, it should be observed that the distribution determined by Teramachi et al. could also be explained by an experimental error of 1–2% in the determination of the chemical composition of copolymer fractions.

Hence, at present there exists some uncertainty in the interpretation of experimental results concerning the statistical chemical heterogeneity of copolymers. The effects under investigation lie at the limit of the potentials offered by the present-day experimental techniques (e.g., of separation procedures and of the determination of chemical composition of copolymers). To obtain reliable experimental data which would provide us with unambiguous conclusions will be no easy task.

Appendix. Distribution Function of Chemical Composition

The marginal distribution function of chemical composition $g(y)$ is obtained by integrating the distribution function (1) over all degrees of polymerization, P

$$g(y) = \int_P f(P,y)\,\mathrm{d}P = (1-\rho)\int_0^\infty \frac{P}{P_\mathrm{n}^{*2}}\exp\left(-\frac{P}{P_\mathrm{n}^{*}}\right)\times \left(\frac{P}{2\pi\bar{w}(1-\bar{w})k}\right)^{1/2}\exp\left(-\frac{Py^2}{2\bar{w}(1-\bar{w})k}\right)\mathrm{d}P + \rho\int_0^\infty \frac{P^2}{2P_\mathrm{n}^{*3}}\exp\left(-\frac{P}{P_\mathrm{n}^{*}}\right)\times \left(\frac{P}{2\pi\bar{w}(1-\bar{w})k}\right)^{1/2}\exp\left(-\frac{Py^2}{2\bar{w}(1-\bar{w})k}\right)\mathrm{d}P = I_1 + I_2 \qquad \text{(A-1)}$$

The first integral, I_1, is related to the distribution function of chemical composition for the termination by disproportionation and was solved by Stockmayer[9] for the case $\rho = 0$ with a result given by eq 3. For nonzero ρ we have

$$I_1 = \frac{3}{4}(1-\rho)\frac{\Xi}{(1+z^2)^{5/2}} \qquad \text{(A-2)}$$

where Ξ is given by eq 6.

The solution of the second integral, I_2, which corresponds to termination by recombination, reduces to the calculation of the improper integral of the standard type $\int_0^\infty x^r \exp(-ax)\,\mathrm{d}x$; on introducing substitution (6), we obtain

$$I_2 = \frac{15}{16}\rho\frac{\Xi}{(1+z^2)^{7/2}} \qquad \text{(A-3)}$$

The sum of relations (A-2) and (A-3) then yields eq 5 (cf. ref 10). Variance of chemical composition, σ^2, may be calculated from the definition of this quantity

$$\sigma^2 = \int_y (y-\bar{y})^2 g(y)\,\mathrm{d}y \qquad \text{(A-4)}$$

The mean value of deviations of composition from the mean composition, $\bar{y}$, is nil. Using eq 5 and 6, we have

$$\sigma^2 = \frac{3(1-\rho)}{4\Xi^2}\int_z \frac{z^2}{(1+z^2)^{5/2}}\,\mathrm{d}z + \frac{15\rho}{16\Xi^2}\int_z \frac{z^2}{(1+z^2)^{7/2}}\,\mathrm{d}z = I_1^* + I_2^* \qquad \text{(A-5)}$$

Because of the very small width of the distribution function $g(y)$, the integration range of y (or z) may be extended[9] from $-\infty$ to $+\infty$. The improper integrals in eq A-5 are again of the standard type. The calculation of the first integral, I_1^*, for termination by disproportionation, i.e., at $\rho = 0$, leads to eq 10 derived by Leng.[14] In a more general case, it results

$$I_1^* = \frac{(1-\rho)\bar{w}(1-\bar{w})k}{P_\mathrm{n}^*} \qquad \text{(A-6)}$$

Similarly, for the second integral it may be derived that

$$I_2^* = \frac{\rho\bar{w}(1-\bar{w})k}{2P_\mathrm{n}^*} \qquad \text{(A-7)}$$

Substitution into eq A-5 yields the resulting eq 9.

References and Notes

(1) Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781.
(2) Myagchenkov, V. A.; Frenkel', S. Ya. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 2348.
(3) Stejskal, J.; Kratochvíl, P. *J. Appl. Polym. Sci.* **1978**, *22*, 2925.
(4) Stejskal, J.; Kratochvíl, P. *J. Appl. Polym. Sci.* **1980**, *25*, 407.
(5) Teramachi, S.; Kato, Y. *J. Macromol. Sci.—Chem.* **1970**, *4*, 1785.
(6) Teramachi, S.; Kato, Y. *Macromolecules* **1971**, *4*, 54.
(7) Teremachi, S.; Hasegawa, A.; Akatsuka, M.; Yamashita, A.; Takemoto, N. *Macromolecules* **1978**, *11*, 1206.
(8) Teramachi, S.; Hasegawa, A.; Shima, Y.; Akatsuka, M.; Nakajima, M. *Macromolecules* **1979**, *12*, 992.
(9) Stockmayer, W. H. *J. Chem. Phys.* **1945**, *13*, 199.
(10) Kuchanov, S. I. "Metody Kineticheskich Rastchotov v Chimii Polimerov"; Chimiya: Moskva, 1978; p 241.
(11) Stejskal, J.; Straková, D.; Kratochvíl, P., to be submitted for publication.
(12) Stejskal, J.; Kratochvíl, P. *Macromolecules* **1978**, *11*, 1097.
(13) Bevington, J. C.; Melville, H. W.; Taylor, R. P. *J. Polym. Sci.* **1954**, *14*, 463.
(14) Leng, M. Thèse, Strasbourg, 1962 (from: Lamprecht, J.; Strazielle, C.; Dayantis, J.; Benoît, H. *Makromol. Chem.* **1971**, *148*, 285).