

Comparison of the Instantaneous and Conversion Chemical Heterogeneity of Random Copolymers

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Synopsis

The calculation of a general distribution function of chemical composition of random copolymers involving the instantaneous and conversion chemical heterogeneity is demonstrated. Typical examples offer a semiquantitative view about the effect of the two types of chemical heterogeneity on the shape and width of the distribution of chemical composition.

INTRODUCTION

Copolymers, like most of synthetic macromolecular compounds, are polydisperse with respect to their molecular weight. Unlike homopolymers, the individual macromolecules forming the copolymer may differ not only in their molecular weight but also in their chemical composition. This phenomenon is called chemical heterogeneity.

For random copolymers, the so-called conversion heterogeneity is of particular importance. Its cause consists in a change in the composition of the monomer mixture during copolymerization (if the latter is not azeotropic copolymerization), and thus in a change in the composition of the forming copolymer. The instantaneous heterogeneity originates in the statistical nature of the copolymer chain formation.

The instantaneous heterogeneity is usually neglected compared with the conversion heterogeneity (although this is not always justified) or is discussed separately. Many present experimental methods are sensitive enough to provide principal information also on the instantaneous heterogeneity or may be affected by the latter. We therefore regarded it as useful to make a rough estimate of the extent to which this type of chemical heterogeneity contributes to the total chemical heterogeneity. Some model calculations should enable the reader to get a semiquantitative view of the total chemical heterogeneity of random copolymers.

At any instant of the random copolymerization of two monomers A and B, a copolymer is formed which may be assigned a certain chemical composition w (given in our case by, e.g., the weight fraction of A). This composition depends on the instantaneous composition of the monomer mixture v , and it holds that¹

$$w = \frac{v^2(r_A - t) + vt}{v^2[t(r_B - 1) + r_A - 1] + v(1 - 2r_B t + t) + r_B t} \quad (1)$$

where r_A and r_B are the copolymerization parameters and $t = M_{0A}/M_{0B}$ is the ratio of molecular weights of monomers A and B.

If the copolymerization is carried out at an initial composition of the monomer mixture, v_0 , differing from the azeotropic composition, the composition of the copolymer arising at the given instant of copolymerization depends on conversion ψ . The differential weight distribution function of chemical composition, w , for complete conversions has been derived by Myagchenkov and Frenkel¹:

$$g_C(w) = \left| \left(\frac{v}{v_0} \right)^{k_1} \left(\frac{v-1}{v_0-1} \right)^{k_2} \left(\frac{v-k_4}{v_0-k_4} \right)^{k_3} \left(\frac{k_1}{v} + \frac{k_2}{v-1} + \frac{k_3}{v-k_4} \right) \right. \\ \left. \times \frac{[v^2(r_B t + r_A - 1 - t) + v(1+t - 2r_B t) + r_B t]^2}{v^2(r_A + r_B t^2 - 2r_A r_B t) + 2v t r_B (r_A - t) + r_B t^2} \right| \quad (2)$$

where

$$k_1 = \frac{r_B}{1-r_B} \quad k_2 = \frac{r_A}{1-r_A} \\ k_3 = \frac{1-r_A r_B}{(r_A-1)(1-r_B)} \quad k_4 = \frac{t(1-r_B)}{t(1-r_B) + (1-r_A)}$$

The relation between the instantaneous composition of the monomer mixture and the copolymer composition is given by eq. (1). At incomplete conversions of copolymerization, $\psi < 1$, the distribution function (2) must be normalized by the factor $1/\psi$.

Owing to the statistical nature of formation of the copolymer chain, the chemical composition of the individual copolymer macromolecules, w_i , formed at the same instant of copolymerization is generally different. Thus, the chemical composition w is an average instantaneous composition of the copolymer. The relative weight content of macromolecules with composition within the interval w_i , ($w_i + dw_i$) or exhibiting a deviation from the average instantaneous composition w from the interval ($w_i - w$), ($w_i - w$) + $d(w_i - w)$ may be described by the differential weight distribution function derived by Stockmayer²:

$$g_S(w_i - w | w) = \frac{3\bar{Z}}{4[1 + \bar{Z}^2(w_i - w)^2]^{5/2}} \quad (3)$$

where

$$\bar{Z}^2 = \frac{M_n}{2M_0 w(1-w)\xi}$$

and

$$\xi = [1 - 4w(1-w)(1 - r_A r_B)]^{1/2}$$

where M_n is the number-average molecular weight of the copolymer and M_0 is the molecular weight of the monomer unit. The expression for $g_S(w_i - w | w)$ is obtained in the closed form only if M_0 is identical for both monomers, i.e., $t = 1$.

By denoting the distribution function $g_S(w_i - w | w)$ as a conditional function, we want to stress that the latter describes the instantaneous heterogeneity of the copolymer formed at a given instant of copolymerization, whose instantaneous average composition equals just w . The distribution function of the compositional deviations $g_S(w_i - w | w)$ is even, which is advantageous for

mathematical reasons; the distribution function of chemical composition $g_S(w_i|w)$ has a similar form, but it is shifted along the axis of abscissa and is symmetrical about the average value w .

The distribution function $g_C(w)$ reflects conversion heterogeneity. This distribution function would describe the real distribution of chemical composition only if the molecular weight of copolymer chains would approach infinity, and the effect of instantaneous heterogeneity would not show up. As may further be derived from eq. (8), the width of the distribution function $g_S(w_i - w|w)$ decreases with increasing molecular weight of the copolymer. For an infinite molecular weight, this width is zero. On the other hand, the distribution function $g_S(w_i - w|w)$ would describe the total chemical heterogeneity only if the function $g_C(w)$ were of zero width, i.e., if w were constant. This is fulfilled either for an azeotropic copolymerization or for a copolymerization led to an infinitesimally low conversion.

THEORETICAL

General Distribution Function of Chemical Composition

The general distribution function of chemical composition, $g(w_i)$, of a random copolymer with finite molecular weight prepared to nonzero conversion is obtained by integrating the distribution function $g_S(w_i|w)$ over all compositions w ,

$$g(w_i) = \int_w g_S(w_i|w)g_C(w) dw \quad (4)$$

where the function $g_C(w)$ has the meaning of statistical weight function.

With respect to the relatively complex form of distribution functions on the right-hand side of eq. (4), the integration must be carried out numerically. Some restrictions should be pointed out. Since the distribution function (3) was derived assuming equality of the molecular weights of monomer units, eq. (4) holds only under the same condition. (This assumption need not be introduced if, for example, the number distribution functions were used. Most of experimentally available characteristics of copolymers, however, are derived from weight distribution functions; e.g., for a chemically heterogeneous sample, the experimentally determined composition of the copolymer is the weight average of chemical composition, etc.) Also, in eq. (3) there appears the molecular weight M_n of a copolymer formed at the given instant of copolymerization. This molecular weight may vary in the course of copolymerization, and in the integration according to eq. (4) one should respect its dependence on w .

Statistical Variance of Chemical Composition

The width of distribution of the chemical composition may be characterized, for example, by its variance:

$$D(w_i) = \int_{w_i} (w_i - \bar{w})^2 g(w_i) dw_i \quad (5)$$

where the total average (i.e., experimentally available) composition of the copolymer, \bar{w} , is given by

$$\bar{w} = \int_{w_i} w_i g(w_i) dw_i = \int_w w g_C(w) dw \quad (6)$$

In principle, it is formally possible to introduce partial variances of chemical composition, corresponding to the conversion chemical heterogeneity,

$$D_C(w) = \int_w (w - \bar{w})^2 g_C(w) dw = \overline{w^2} - (\bar{w})^2 \quad (7)$$

and a variance corresponding to the instantaneous heterogeneity at a given instant of copolymerization (i.e., at the instantaneous average composition being just w) (Appendix A):

$$D_S(w_i|w) = \int_{w_i} (w_i - w)^2 g_S(w_i|w) dw_i = \frac{M_0}{M_n} w(1-w)\xi \quad (8)$$

For the total variance of chemical composition, the equation (Appendix B)

$$D(w_i) = D_C(w) + \int_w D_S(w_i|w) g_C(w) dw \quad (9)$$

can be derived. The integral on the right-hand side is the "average" variance of chemical composition corresponding to the instantaneous heterogeneity.

For the upper estimate of the total variance, the equation

$$D(w_i) \leq D_C(w) + \Omega_S \quad (10)$$

may be used, in which Ω_S represents the maximum value of the integral in eq. (9). It may be shown³ that

$$\Omega_S = \frac{M_0}{M_n} \frac{(r_A r_B)^{1/2}}{4} \quad \text{for } r_A r_B \geq \frac{1}{3}$$

$$\Omega_S = \frac{M_0}{M_n} \frac{\sqrt{3}}{18(1 - r_A r_B)} \quad \text{for } r_A r_B \leq \frac{1}{3} \quad (11)$$

RESULTS AND DISCUSSION

Model calculations of the general distribution functions of chemical composition were performed with the copolymerization parameters $r_A = r_B = 0.5$ and with the molecular weights of monomer units $M_{0A} = M_{0B} = 100$ (Fig. 1). These parameters approximately correspond to, for example, the monomer pair styrene-methyl methacrylate. The potential dependence of molecular weight M_n of the forming copolymer on the conversion of copolymerization was not considered. The initial composition of the monomer mixture, $v_0 = 0.25$, was chosen to be sufficiently different from that of the azeotropic mixture ($v_0^{az} = 0.50$).

At zero or infinitesimal conversion of copolymerization, the distribution of chemical composition is given only by the instantaneous heterogeneity. The distribution functions are symmetrical, Figure 1(a). The width of distribution quickly decreases with increasing molecular weight of the copolymer, Table I, also eq. (8). A copolymer with an infinite molecular weight would be chemically homogeneous; its distribution function is represented in Figure 1(a) by a per-

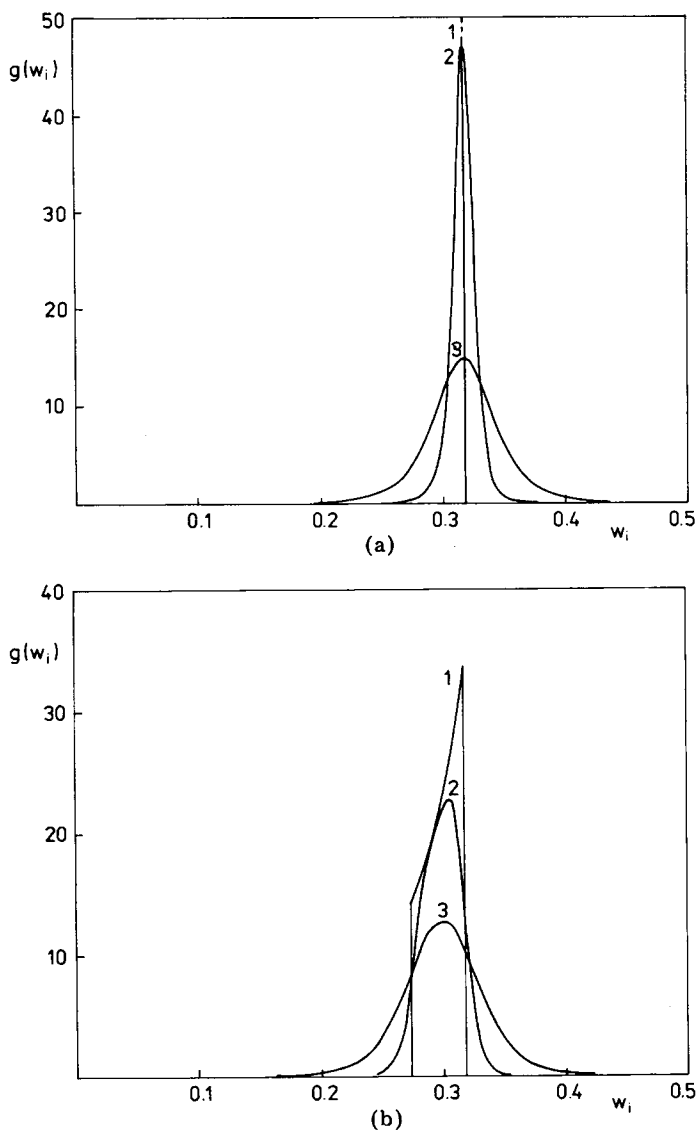


Fig. 1. Distribution function of chemical composition, $g(w_i)$, of a model random copolymer with molecular weight $M_n = \infty$, 10^5 , and 10^4 (curves 1, 2, and 3, respectively) prepared up to weight conversion $\psi = 0$ (a), 0.5 (b), and 0.9 (c).

pendicular straight line of zero width. Figure 1(a) also shows that, if the molecular weight is sufficiently low (order of magnitude 10^4), the copolymerization product contains a nonnegligible amount of chains differing in their chemical composition by as much as 20 wt % A. Thus, the chemical heterogeneity of such low molecular weight samples cannot be neglected.

With increasing conversion, the effect of conversion chemical heterogeneity becomes operative, and the distribution functions broaden. The instantaneous heterogeneity may still predominate for low molecular weight samples, Figure 1(b), Table I. Finally, at high conversions the total chemical heterogeneity is

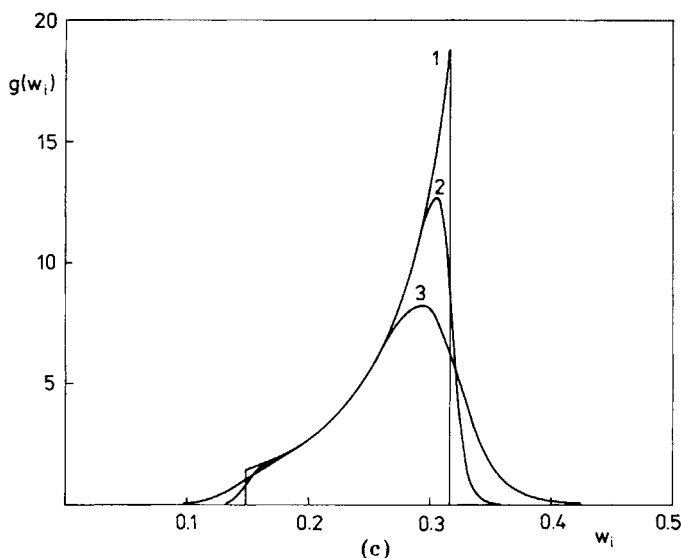


Fig. 1. (Continued from previous page.)

given mostly by the conversion heterogeneity. In this case, too, the effect of instantaneous heterogeneity on the broadening of distribution functions is easy to see, Figure 1(c).

Table I summarizes the individual partial variances of chemical composition and the total variance of chemical composition; the total variance of chemical composition is compared with its upper estimate calculated according to eq. (10). Numerical calculations show that in applications the "average" instantaneous variance of chemical composition given by the integral on the right-hand side of eq. (9) may be approximated by the variance $D_S(w_i|\bar{w})$. This value may be

TABLE I
Dependence of Variance of Chemical Composition of a Random Copolymer, $D_C(w)$,
Corresponding to Conversion Heterogeneity, and of Total Variance, $D(w_i)$, on Conversion ψ and
Molecular Weight M_n^a

ψ	\bar{w}	M_n	$D_C(w)$	$D(w_i)$	$10^4 \times$	
					$D_C(w) + \Omega_S^b$	$D_C(w) + D_S(w_i \bar{w})^c$
0	0.318	∞	0	0	0	0
		10^5		1.28	1.28	1.28
		10^4		12.8	12.8	12.8
0.5	0.299	∞	1.63	1.63	1.63	1.63
		10^5		2.85	2.91	2.91
		10^4		13.5	14.4	14.4
0.9	0.268	∞	18.4	18.4	18.4	18.4
		10^5		19.6	19.7	19.7
		10^4		30.3	31.2	31.0

^a Where \bar{w} is the average copolymer composition, Ω_S is the upper estimate of variance corresponding to instantaneous heterogeneity according to eq. (11), $D_S(w_i|\bar{w})$ has been calculated according to eq. (8), $\nu_0 = 0.25$, $r_A = r_B = 0.5$, and $M_{0A} = M_{0B} = 100$.

^b Upper estimate of total variance according to eq. (10).

^c Estimate of total variance according to eq. (9) using the approximation $\int_w D_S(w_i|w) g_C(w) dw \approx D_S(w_i|\bar{w})$.

calculated using eq. (8) after substitution of the total average composition of the copolymer \bar{w} for the instantaneous average composition, w (Table I). Also, the comparatively easily obtained sum $D_c(w) + \Omega_S$ seems to be a good approximation of $D(w_i)$.

Results of the above model calculations cannot be mechanically generalized to apply to any copolymer. The participation of instantaneous and conversion chemical heterogeneity may vary from one case to another and is given especially by values of the copolymerization parameters, by the initial composition of the monomer mixture, and by conversion. In this work, we attempted to demonstrate on a typical example the possible extent of both types of chemical heterogeneity. An analysis shows that change in the relevant parameters characterizing copolymerization is not likely to produce any essential change in the total image; the trend of quantitative changes may usually be estimated by reasoning. The effect of instantaneous heterogeneity on the width of distribution of chemical composition and on its form, particularly with low molecular weight copolymers, should be taken into account, e.g., in the interpretation of the results of fractionation according to chemical composition or in the analysis of results obtained by GPC and/or light scattering.

APPENDIX A

Variance Corresponding to the Instantaneous Heterogeneity of Chemical Composition

The variance is defined by

$$D_S(w_i|w) = D_S(w_i - w|w) = \int_{w_i-w} [(w_i - w) - \overline{(w_i - w)}]^2 g_S(w_i - w|w) d(w_i - w|w) \quad (\text{A-1})$$

Since $\overline{(w_i - w)} = 0$, after substitution from eq. (3) it holds that

$$D_S(w_i|w) = \frac{3}{4} \int_{w_i-w} (w_i - w)^2 \frac{\Xi d(w_i - w)}{[1 + \Xi^2(w_i - w)^2]^{5/2}} \quad (\text{A-2})$$

After substitution $x = \Xi^2(w_i - w)^2$ and expansion of the integration range of deviations² $(w_i - w)$ from $-\infty$ to $+\infty$, we obtain (assuming that M_n is independent of composition w) after rearrangement

$$D_S(w_i|w) = \frac{3}{4\Xi^2} \int_0^\infty \frac{x^{1/2}}{(1+x)^{5/2}} dx = \frac{3}{4\Xi^2} \frac{\Gamma\left(\frac{3}{2}\right)\Gamma(1)}{\Gamma\left(\frac{5}{2}\right)} = \frac{1}{2\Xi^2} \quad (\text{A-3})$$

$$D_S(w_i|w) = \frac{M_0 w(1-w)\xi}{M_n} \quad (8)$$

APPENDIX B

Total Variance of Chemical Composition

For the total variance of chemical composition, $D(w_i)$, we obtain

$$\begin{aligned}
 D(w_i) &= \int_{w_i} (w_i - \bar{w})^2 g(w_i) dw_i \\
 &= \int_{w_i} \int_w (w_i - \bar{w})^2 g_S(w_i|w) g_C(w) dw dw_i \\
 &= \int_w \left[\int_{w_i} w_i^2 g_S(w_i|w) dw_i \right] g_C(w) dw - (\bar{w})^2 \quad (\text{B-1})
 \end{aligned}$$

It holds, also, that

$$D_S(w_i|w) = \int_{w_i} (w_i - w)^2 g_S(w_i|w) dw_i = \int_{w_i} w_i^2 g_S(w_i|w) dw_i - w^2 \quad (\text{B-2})$$

Substitution of (B-2) into (B-1) yields

$$\begin{aligned}
 D(w_i) &= \int_w D_S(w_i|w) g_C(w) dw + \int_w w^2 g_C(w) dw - (\bar{w})^2 \\
 &= \int_w D_S(w_i|w) g_C(w) dw + \overline{w^2} - (\bar{w})^2 \\
 &= \int_w D_S(w_i|w) g_C(w) dw + D_C(w)
 \end{aligned} \quad (9)$$

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Received November 15, 1978

Revised September 10, 1979