relaxation mechanisms. The first relaxation mode is characteristic of the motion of the copolymer as a whole. The second mode is due to the internal concentration fluctuations. We have shown that it is possible from an experimental point of view to detect these motions in one experiment. We hope to be able in the near future to see if there is agreement between these theoretical results and experiments.

Acknowledgment. We want to express our gratitude to Professor A. Z. Akcasu for having initiated this study. We thank Dr. C. Picot for many helpful discussions.

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Statistical Chemical Heterogeneity of Copolymers. Modification of the Stockmayer Distribution Function of Chemical Composition

Jaroslav Stejskal* and Pavel Kratochvil

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received February 5, 1987*

ABSTRACT: The distribution function of chemical composition describing the statistical chemical heterogeneity of statistical copolymers derived by Stockmayer is adapted to cover the case of (a) copolymers with any Schulz–Zimm distribution of degrees of polymerization and (b) copolymers with monomeric units of different molecular weights. The variance of the molar chemical composition is independent of the width of distribution of degrees of polymerization. The derived expressions can be applied to graft copolymers prepared by statistical copolymerization of an ordinary monomer with a macromonomer. In this case, the chemical composition distributions are asymmetrical and much broader than those of common statistical copolymers with identical average composition.

Introduction

The statistical chemical heterogeneity of copolymers prepared by statistical copolymerization of two monomers, A and B, which can be described in terms of the simple scheme with two monomer reactivity ratios, r_A and r_B, has been analyzed by Stockmayer in his classical paper.[1] The two-dimensional differential weight distribution[2] of degrees of polymerization P and of deviations $y = F - \bar{F}$ of the chemical composition of the individual chains, F, from the average copolymer composition, $\bar{F}$, was derived as

$$W(P,y) = \left[\frac{P}{P_n^{\,2}}\exp\left(-\frac{P}{P_n}\right)\right]\left[\frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{y^2}{2\sigma^2}\right)\right] \qquad (1)$$

on assumption that the termination is by disproportionation. A similar equation has also been derived[1] for a case when recombination of radicals is involved. P_n is the number-average degree of polymerization and the parameter σ^2 is defined by

$$\sigma^2 = \frac{\bar{F}(1-\bar{F})k}{P} \qquad (2)$$

where

$$k = [1 + 4\bar{F}(1-\bar{F})(r_Ar_B - 1)]^{1/2} \qquad (3)$$

The compositions F and $\bar{F}$ are expressed in mole fractions of component A.

The distribution function (eq 1) describes the statistical (also called instantaneous or natural) chemical heterogeneity of statistical copolymers. It does not cover the effect of chemical heterogeneity caused by a drift in the composition of the monomer mixture with conversion during copolymerization.[3] Function 1 formally consists of two factors. The first one is immediately recognized as the weight distribution of degrees of polymerization for a polymer prepared by a polymerization where termination of growing chains occurs entirely by disproportionation, i.e., as the most probable distribution,

$$W(P) = \frac{P}{P_n^{\,2}}\exp\left(-\frac{P}{P_n}\right) \qquad (4)$$

The second factor represents a normal (Gaussian) distribution,

$$W(y|P) = \frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{y^2}{2\sigma^2}\right) \qquad (5)$$

and states that the compositions of chains of a given degree of polymerization, P, are normally distributed about the mean value with standard deviation σ. Function 5 is denoted here as a conditional distribution function, $W(y|P)$, i.e., as the distribution of deviations y on condition, that the degree of polymerization has a value of P.

By integration of the two-dimensional function 1 over all degrees of polymerization, P, Stockmayer derived also

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the marginal distribution of compositional deviations,[1]

$$W(y)\,\mathrm{d}y = \frac{3\,\mathrm{d}z}{4(1+z^2)^{5/2}} \tag{6}$$

where

$$z^2 = \frac{P_n y^2}{2\bar{F}(1-\bar{F})k} \tag{7}$$

For the case of copolymerization where termination occurs by recombination, an analogous distribution function was derived.[4,5]

In recent years, a new class of statistical copolymers prepared by copolymerization of low molecular weight monomers with macromonomers has been attracting much attention.[6] This type of synthesis leads to well-defined graft copolymers. The aim of the present contribution is to modify the above equations and thus extend their applicability to the statistical copolymers involving comonomers with highly different molecular weights. We shall also treat a more general case when the degrees of polymerization of a statistical copolymer obey the empirical Schulz–Zimm distribution and not just its particular case given by eq 4.

Theoretical Section

The Stockmayer distributions 1 and 6 can be modified in two steps. In the first step, the most probable distribution of degrees of polymerization 4 is replaced by a more general empirical Schulz–Zimm distribution (Γ-distribution)

$$W(P) = \frac{b^{a+1}}{\Gamma(a+1)} P^a \exp(-bP) \tag{8}$$

Parameters a and b are related to the number and weight-average degrees of polymerization, P_n and P_w, by

$$a = \left(\frac{P_w}{P_n} - 1\right)^{-1} \tag{9}$$

and

$$b = \frac{a}{P_n} = \frac{a+1}{P_w} \tag{10}$$

$\Gamma(a+1)$ is the gamma function; for a positive integer a, the relation $\Gamma(a+1) = a!$ holds. Distribution 8 reduces to distribution 4 for $a = 1$, i.e., for $P_w/P_n = 2$.

After introduction of the Schulz–Zimm distribution 8 instead of distribution 4 into the two-dimensional distribution function 1 and after integration over all degrees of polymerization, P, we obtain (Appendix 1)

$$W(y)\,\mathrm{d}y = \frac{\Gamma\left(a+\frac{3}{2}\right)}{\Gamma(a+1)\Gamma(1/2)} \frac{\mathrm{d}z}{(1+z^2)^{a+(3/2)}} \tag{11}$$

where now

$$z^2 = \frac{P_n y^2}{2ak\bar{F}(1-\bar{F})} \tag{12}$$

This distribution can be used for a description of the statistical chemical heterogeneity of a statistical copolymer with any value of ratio $P_w/P_n = (a+1)/a$, e.g., for an azeotropic copolymer prepared up to a finite conversion.

The variance of chemical composition is given by (Appendix 2)

$$\sigma_w^2 = \frac{\bar{F}(1-\bar{F})k}{P_n} \tag{13}$$

i.e., by an expression closely related to eq 2. It is interesting to note that the variance, σ_w^2, which is a measure of the width of chemical composition distribution, does not depend on parameter a and is thus independent of P_w/P_n.

The relation between the mole fraction of component A in a copolymer chain and its weight fraction, x, is

$$F = \frac{x}{(1-t)x + t} \tag{14}$$

where $t = M_{0A}/M_{0B}$ is the ratio of molecular weights of the monomeric units A and B, respectively. If we introduce the chemical composition x into distribution function 11 by using eq 14 and use eq 14 to relate also the average values of chemical composition, $\bar{F}$ and $\bar{x}$, we obtain the differential weight distribution of chemical composition in the same formal layout as in eq 11,

$$W(x) = \frac{\Gamma\left(a+\frac{3}{2}\right)}{\Gamma(a+1)\Gamma(1/2)} \frac{1}{(1+z^2)^{a+(3/2)}} \frac{\mathrm{d}z}{\mathrm{d}x} \tag{15}$$

The parameters of this distribution are now defined as

$$z^2 = \frac{P_n t}{2ak\bar{x}(1-\bar{x})} \frac{(x-\bar{x})^2}{[(1-t)x+t]^2} \tag{16}$$

$$k = \left[1 + \frac{4t\bar{x}(1-\bar{x})}{[(1-t)\bar{x}+t]^2}(r_A r_B - 1)\right]^{1/2} \tag{17}$$

and

$$\frac{\mathrm{d}z}{\mathrm{d}x} = \left(\frac{P_n t}{2ak\bar{x}(1-\bar{x})}\right)^{1/2} \frac{(1-t)\bar{x}+t}{[(1-t)x+t]^2} \tag{18}$$

For $t = 1$, i.e., for identical molecular weights of monomeric units, eq 15–17 reduce to eq 3, 11, and 12. To evaluate the chemical composition distribution according to eq 15, one has to know the ratio of molecular weights of monomeric units, t, the number-average degree of polymerization, P_n, the P_w/P_n ratio, the average composition of the copolymer, $\bar{x}$ (weight fraction of component A), and the monomer reactivity ratios or their product, $r_A r_B$. All these parameters are usually available or can be obtained experimentally.

Results and Discussion

Common Statistical Copolymers. With decreasing degrees of polymerization, P_n, the chemical composition distribution (CCD) broadens (Figure 1a) and the statistical chemical heterogeneity increases, as reflected by an increase of variance σ_w^2 (eq 13). The copolymer is chemically homogeneous only at infinite degrees of polymerization. A similar trend, i.e., the broadening of CCD, is observed with an increase in the product of monomer reactivity ratios, $r_A r_B$, i.e., with increasing tendency to formation of long sequences of identical monomeric units. Only a strictly alternating copolymer is chemically homogeneous. In this case, $r_A r_B = 0$ and $\bar{F} = 0.5$, and parameter k and thus also variance σ_w^2 reduce to zero.

Figure 2 illustrates the effect of the copolymer nonuniformity in degrees of polymerization on the shape of CCD. For a uniform copolymer, $P_w/P_n = 1$ and the CCD is Gaussian according to eq 5. For copolymers with $P_w/P_n > 1$, CCD is given by eq 11. One might be tempted to conclude that CCD becomes broader with decreasing P_w/P_n; however, the variance, σ_w^2, of all three CCD drawn in Figure 2 is the same, due to eq 13. This observation is easily understood. From eq 2, we see that macromolecules

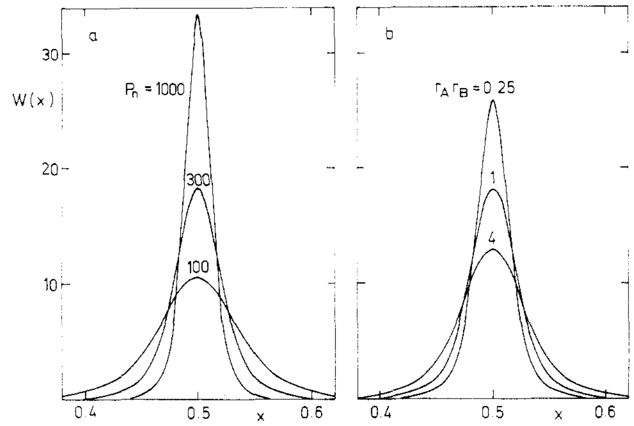

Figure 1. Differential weight distribution, $W(x)$, of chemical composition, x, of the statistical copolymers calculated according to Stockmayer for (a) different number-average degrees of polymerization, P_n (while $r_Ar_B = 1$), and (b) for different products of monomer reactivity ratios, r_Ar_B (at constant $P_n = 300$). Copolymers are assumed to have the most probable distribution of degrees of polymerization, $P_w/P_n = 2$, the same molecular weights of monomer units, $t = 1$, and the same average chemical composition, $\bar{x} = 0.5$.

with low P have a high σ^2 and vice versa. Let us increase the nonuniformity of a copolymer, i.e., broaden the distribution of degrees of polymerization at fixed P_n. Then an increase of σ_w^2 due to the presence of copolymer chains with low P is compensated for by an equivalent decrease of σ_w^2 caused by macromolecules with high P, which have to be present in order to keep P_n constant.

Statistical Copolymers Prepared from Macromonomers. At first sight, the second step in the modification of the Stockmayer distribution function, i.e., its expression in terms of weight fractions of monomer units instead of mole fractions, might be regarded as a rather formal operation. However, this step enables us to predict CCD even for statistical copolymers of a low molecular weight monomer with a macromonomer.

When graft copolymers are prepared by the macromonomer method, the mole fraction of macromonomer units in the copolymer is usually very low (a few mole percent). In this case, the incorporation of macromonomer units can usually be regarded as random, and if the monomer reactivity ratios are not known, the approximation $r_Ar_B = 1$ seems to be justified.[6]

Figure 3 shows an example of CCD for various ratios of molecular weights of a low molecular weight monomer, A, and of a macromonomer, B, $t = M_{0A}/M_{0B} = 1, 0.01, 0.005$, and 0.001; for molecular weight of the monomer $M_{0A} = 100$, this corresponds to molecular weights of the macromonomer $M_{0B} = 100, 10\,000, 20\,000$, and 100 000, respectively (the macromonomer is assumed to be uniform in molecular weight). Curve 1 represents the classical Stockmayer CCD for copolymers with equal molecular weight of the monomer units. This CCD is symmetrical with respect to the average chemical composition and, in accord with expectation, is also fairly narrow. If under similar conditions a macromonomer is copolymerized, CCD is substantially broader and asymmetrical (curves 2–4), the higher the molecular weight of the macromonomer.

It can be shown that, similarly to common statistical copolymers, also in this case CCD narrows when the degree of polymerization of the backbone, formed prevailingly by low molecular weight monomeric units, increases. However, the chemical heterogeneity of copolymers prepared from macromonomers is always substantially larger compared to the ordinary statistical copolymers with the same degree of polymerization and weight composition.

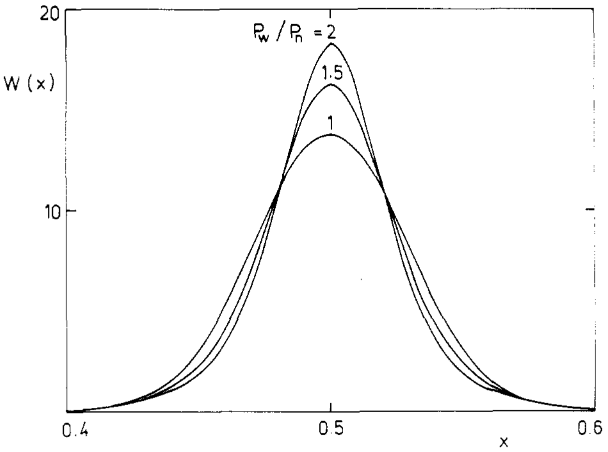

Figure 2. Effect of the P_w/P_n value on the shape of CCD $W(x)$. Calculated for degree of polymerization $P_n = 300$ and equal weight content of both monomeric units, $\bar{x} = 0.5$, with identical molecular weight, $t = 1$, which are randomly distributed, $r_Ar_B = 1$, in the chains.

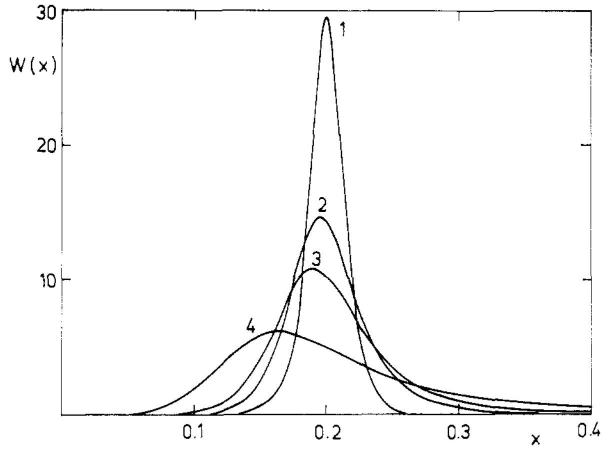

Figure 3. Dependence of the shape of CCD $W(x)$ on the ratio of molecular weights of monomeric units, $t = M_{0A}/M_{0B}$. Calculated for the degree of polymerization (of the backbone in case of graft copolymers) $P_n = 500$ and the average weight composition $\bar{x} = 0.2$, assuming random formation of the copolymer chain, $r_Ar_B = 1$, and the most probable distribution of degrees of polymerization, $P_w/P_n = 2$. $t = 1$ (1), 0.01 (2), 0.005 (3), and 0.001 (4).

In our recent paper,[7] the differential weight CCD for a graft copolymer has been derived for the case where a backbone with the most probable distribution of degrees of polymerization carries monodisperse grafts,

$$W(x) = \frac{r^2\bar{x}}{1 - r^2\bar{x}}\left(\frac{1-\bar{x}}{(1-r)\bar{x}} + Q\right)\sum_{m=1}^{\infty} m^2\frac{[m(1-r)Q\exp(-Q)]^m}{m!}\,\frac{dQ}{dx} \tag{19}$$

where

$$Q = \frac{1}{1-r}\,\frac{(1-\bar{x})x}{\bar{x}(1-x)} \tag{20}$$

and $r = 1/(m_n + 1)$, m_n being the average number of grafts in a copolymer macromolecule and $\bar{x}$ the average weight composition. The derivation of this CCD is based on the statistics of random coupling of grafts to backbones.

In Figure 4, two CCD calculated by using eq 15 and 19 are compared for one of the examples discussed earlier.[7] Although the statistical aproaches to the derivation of these functions have been different, agreement in the shape of both CCD may be regarded as good, certainly well within the limits of error in the potential experimental

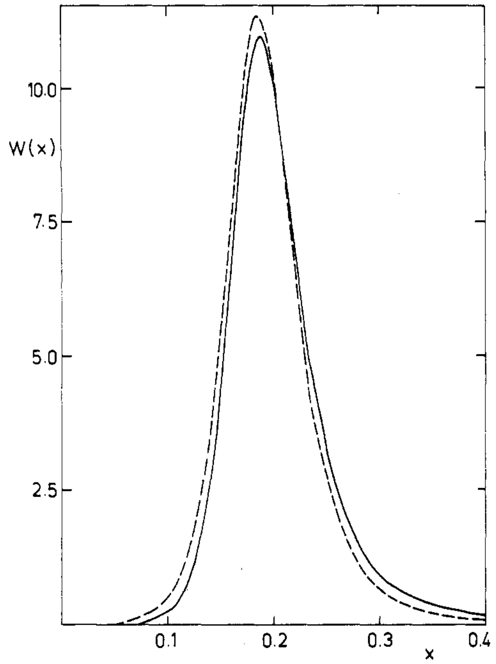

Figure 4. Comparison of CCD $W(x)$ of a graft copolymer prepared from a monomer and a macromonomer calculated by the present method according to eq 15 (full curve) and by a different statistical approach[7] according to eq 19 (dashed line). Calculated for $P_n = 500$, $P_w/P_n = 2$, $t = 0.005$, $r_A r_B = 1$, and $\bar{x} = 0.198$ ($r = 0.091$, i.e., the average number of grafts $m_n = 10$).

determination. The present method of calculation of CCD using eq 15 based on the Stockmayer equation may be easier to handle, especially for relatively high degrees of grafting (approximately $m_n > 10$), when the series in eq 19 converges slowly. On the other hand, use of eq 15 cannot be recommended for copolymers with very low degrees of grafting, because then the assumptions made in the derivation of eq 1 may not be fulfilled. In that case, the application of eq 19 is more justified.

The attempts at experimental determination of the statistical chemical heterogeneity have gradually been appearing in the literature, along with the improvements of existing experimental techniques or with the introduction of new separation methods. Teramachi and Kato[8] used the cross-fractionation to determine CCD of an azeotropic styrene–methyl methacrylate copolymer, the present authors[5] cross-fractionated sytrene–(2-methoxyethyl methacrylate) copolymer. Teramachi et al.[9] with styrene–methyl methacrylate copolymers and recently Sato et al.[10] with styrene–methyl methacrylate copolymers analyzed CCD by high-performance liquid chromatography using the gradient-elution method. Also, combination of other chromatographic methods[11] could be an efficient tool to characterize CCD due to the statistical chemical heterogeneity. The extent of the statistical heterogeneity of common statistical copolymers is usually small, and its characterization, even by the most sensitive modern methods, is a serious problem. On the other hand, with graft copolymers prepared from macromonomers, where the expected statistical heterogeneity is more pronounced, the experimental verification of theoretical prediction might be easier.

Appendix 1. Chemical Composition Distribution

The integration of the two-dimensional distribution function $W(P,y)$ over all degrees of polymerization, P, yields the marginal distribution of chemical composition in terms of deviations, y, from the average composition,

$$W(y) = \int_0^\infty W(P,y)\,\mathrm{d}P \qquad \text{(A1-1)}$$

Generally, $W(P,y) = W(P)W(y|P)$. After substitution from eq 8 and 5 and rearrangement, we get

$$W(y) = \frac{b^{a+1}}{\Gamma(a+1)}[2\pi\bar{F}(1-\bar{F})k]^{-1/2} \times \int_0^\infty P^{a+(1/2)} \exp\left[-\left(\frac{y^2}{2\bar{F}(1-\bar{F})k} + b\right)P\right]\mathrm{d}P \qquad \text{(A1-2)}$$

For any positive parameters A and B,

$$\int_0^\infty P^A \exp(-BP)\,\mathrm{d}P = \frac{\Gamma(A+1)}{B^{A+1}} \qquad \text{(A1-3)}$$

Eq A1-2 can be rewritten as

$$W(y) = \frac{\Gamma\left(a+\frac{3}{2}\right)}{\Gamma(a+1)\Gamma(1/2)}[2bk\bar{F}(1-\bar{F})]^{-1/2} \times \left(1 + \frac{y^2}{2bk\bar{F}(1-\bar{F})}\right)^{-(a+(3/2))} \qquad \text{(A1-4)}$$

where $\Gamma(1/2) = \pi^{1/2}$. Parameter b is replaced by a/P_n according to eq 10. From eq 12 we have that

$$\frac{\mathrm{d}z}{\mathrm{d}y} = \left(\frac{P_n}{2ak\bar{F}(1-\bar{F})}\right)^{1/2} \qquad \text{(A1-5)}$$

Substituting a new variable z for y according to eq 12 into eq A1-4 and respecting eq A1-5, eq 11 in the text is obtained.

Appendix 2. Statistical Variance of Chemical Composition

The statistical variance, σ_w^2, of chemical composition, F, is defined as

$$\sigma_w^2 = \int_P\int_F (F-\bar{F})^2 W(P,F)\,\mathrm{d}F\,\mathrm{d}P \qquad \text{(A2-1)}$$

or, in terms of compositional deviations $y = F - \bar{F}$, since $\mathrm{d}F = \mathrm{d}y$,

$$\sigma_w^2 = \int_P\int_y y^2\, W(P,y)\,\mathrm{d}y\,\mathrm{d}P \qquad \text{(A2-2)}$$

Using the general relation for the conditional distribution function, $W(P,y) = W(P)W(y|P)$, we can write

$$\sigma_w^2 = \int_P W(P)\left[\int_y y^2\, W(y|P)\,\mathrm{d}y\right]\mathrm{d}P \qquad \text{(A2-3)}$$

Because the integral in square brackets is the variance of normal distribution 5, given by eq 2,

$$\sigma_w^2 = \bar{F}(1-\bar{F})k \int_P \frac{1}{P}\, W(P)\,\mathrm{d}P \qquad \text{(A2-4)}$$

Applying the relation between the number and weight distribution functions of degrees of polymerization, $N(P)$ and $W(P)$,

$$W(P) = \frac{P}{P_n}N(P) \qquad \text{(A2-5)}$$

eq 13 in the text is obtained.

Note Added in Proof

Recently, Tacx has correctly pointed out[12] that, if the molecular weights of monomeric units M_{0A} and M_{0B} differ,

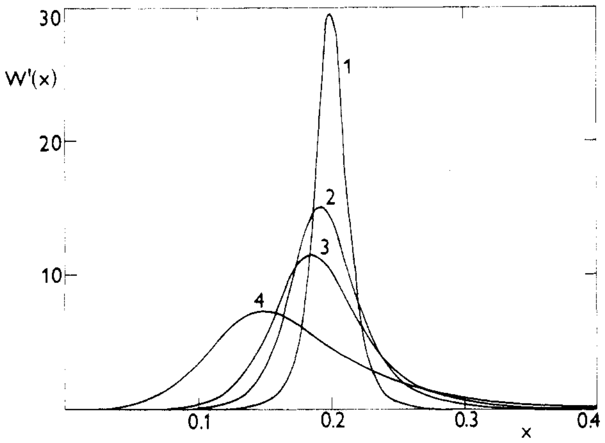

Figure 3'. Modified distribution functions $W'(x)$ corresponding to distribution functions $W(x)$ shown in Figure 3.

i.e., if $t = M_{oA}/M_{oB} \neq 1$, then the Stockmayer distribution function $W(P,y)$ given by eq 1 for $t = 1$ should be modified as

$$W'(P,y) = V(y)W(P,y) \tag{N1}$$

$$V(y) = 1 + \frac{(t-1)y}{(t-1)\bar{F} + 1} \tag{N2}$$

The introduction of the factor $V(y)$ ensues from the relation between the weight and number distribution functions,[2] $W'(P,y)$ and $N(P,y)$,

$$W'(P,y) = (M/M_n)N(P,y) = V(y)(P/P_n)N(P,y) \tag{N3}$$

where M is the molecular weight and M_n its number average. If the factor $V(y)$ given by eq N2 is expressed in terms of chemical composition F,

$$V(F) = \frac{M_{oA}F + M_{oB}(1-F)}{M_{oA}\bar{F} + M_{oB}(1-\bar{F})} \tag{N4}$$

it is immediately recognized as a ratio of the average molecular weights of monomeric units in the copolymer macromolecules with composition F and in the whole copolymer with the average composition $\bar{F}$.

The same principle applies to the modification of the one-dimensional distribution function of compositional deviations y given by eq 11

$$W'(y) = V(y)W(y) \tag{N5}$$

or to that of the chemical composition x expressed on a weight basis and given by eq 15,

$$W'(x) = V(x)W(x) \tag{N6}$$

$$V(x) = 1 + (t-1)\left[\frac{ak\bar{x}(1-\bar{x})}{P_n t}\right]_z^{1/2} \tag{N7}$$

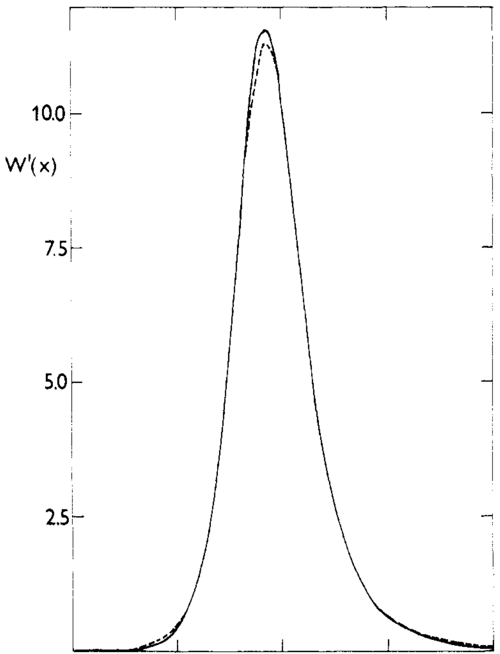

Figure 4'. Modified distribution function $W'(x)$ corresponding to distribution function $W(x)$ shown in Figure 4.

where $z = z(x)$ according to eq 16.

Figures 3' and 4' show the recalculated functions given in Figures 3 and 4. The difference between $W'(x)$ and $W(x)$ may become important when these are broad, i.e., if the number-average degree of polymerization P_n is low and t substantially differs from unity. The use of the modified distribution function $W'(x)$ is more justified and thus should be preferred.

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