

Limits of the Chemical Composition Heterogeneity of Random Copolymers

JAROSLAV STEJSKAL and PAVEL KRATOCHVÍL, *Institute of
Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06
Prague 6, Czechoslovakia*

Synopsis

One of the characteristic features of copolymers is their chemical heterogeneity. Examples are given of the dependence of conversion heterogeneity in the chemical composition of random copolymers on the initial composition of the monomer mixture, along with typical examples of the differential distribution functions of chemical composition. The maximum attainable values of the conversion heterogeneity parameter have been calculated depending on the copolymerization parameters. The conditions are discussed under which copolymers may acquire chemical heterogeneities high enough to be perceived or determined by fractionation or light scattering. Limits are estimated beyond which the chemical heterogeneity becomes undetectably low and the copolymers can be regarded as chemically homogeneous.

INTRODUCTION

Individual chains of copolymer macromolecules can differ from each other not only in their molecular weight but also in the relative content of the individual types of monomer units, i.e., in their chemical composition. Copolymer samples with various chemical heterogeneity can exhibit essentially different properties. For instance, a chemically homogeneous copolymer and a mixture of corresponding homopolymers with the same average composition behave differently in many respects. The cause usually is incompatibility of copolymer chains differing markedly in their chemical composition. Chemical heterogeneity plays an important role in the investigation of the properties of copolymers and is therefore frequently studied.¹

If copolymers are prepared in order to investigate their properties or industrial applications, the product is often demanded to be a "chemically homogeneous" copolymer. The nonnegligible chemical heterogeneity may considerably complicate the interpretation of results of various measurements (e.g., molecular weight determination by light scattering,² sedimentation analysis, or gel permeation chromatography³) or affect the properties of the copolymer (e.g., by a change in mechanical properties^{4,5}). The magnitude of chemical heterogeneity can be checked by one of the experimental methods which should, at least in principle, provide information about the heterogeneity; such methods are, for example, light scattering, fractionation, chromatographic methods, DSC, and some others.

The chemical heterogeneity of random binary copolymers dealt with in this paper has two causes:

1. The statistical heterogeneity originates in the statistical nature of formation of the copolymer chains.⁶ Its magnitude depends on the instantaneous average composition of the forming copolymer, on its degree of polymerization, and thus

also on the copolymerization kinetics. The heterogeneity rapidly decreases with the increasing degree of polymerization and becomes zero for copolymers with an infinite molecular weight. The dependence of statistical heterogeneity on a large number of parameters renders difficult its general analysis.

2. The conversion heterogeneity arises because the composition of the copolymer forming at a given moment of copolymerization generally differs from the composition of the monomeric mixture. With increasing conversion the monomeric mixture becomes richer in one of the monomers, which leads to a change in the copolymer composition in various stages of the reaction.

In the literature, the statistical heterogeneity is mostly neglected compared with the conversion heterogeneity, though this is not always justified. In an actual copolymerization, both mechanisms of formation of chains with different chemical composition are operative simultaneously, and the contributions of the statistical and conversion heterogeneities to the overall chemical heterogeneity cannot be separated from each other.

Since a general calculation of the parameters of chemical heterogeneity is complex, we shall restrict ourselves to the limiting case of copolymers with an infinite molecular weight, for which statistical heterogeneity is zero, and consequently the overall chemical heterogeneity is identical with the conversion heterogeneity. Upper limits of the conversion heterogeneity of random copolymers are estimated in dependence on copolymerization parameters for various conversions. Some restrictions of the validity of conclusions for copolymers with a finite molecular weight are pointed out. It is also discussed with what copolymers the chemical heterogeneity may be so high that it can be determined by light scattering or detected by fractionation, and when the copolymer can be regarded, within the limits of experimental error of these methods, as chemically homogeneous.

THEORETICAL

Distribution functions of the copolymers are generally functions of two variables, dependent both on the chemical composition of copolymer chains, w , and on their molecular weight, M . The differential weight distribution function of chemical composition, $g(w)$, is given by an integral of the corresponding function of two variables, $f(w, M)$, over the whole range of molecular weights. $f(w, M)$ is generally not accessible experimentally; moreover, its determination, if possible at all, would certainly be very time consuming.

Therefore, the chemical heterogeneity of a copolymer is usually described by various parameters which, as a rule, are characteristics of the differential weight distribution function of chemical composition, $g(w)$. In most cases these parameters are related to the variance of the copolymer chemical composition, σ^2 , for which

$$\sigma^2 = \int_w (w - \bar{w})^2 g(w) dw \quad (1)$$

The composition w of a random copolymer poly(A-co-B) is given by the weight fraction of monomeric units A in the copolymer chains;

$$\bar{w} = \int_w w g(w) dw \quad (2)$$

is the overall average copolymer composition. σ^2 has the advantage of being closely connected with some experimentally directly accessible quantities (e.g., heterogeneity parameter Q , see below).

It is difficult to express the distribution function of chemical composition, $g(w)$, in a general way. The literature gives only certain limiting forms of distribution functions. Thus, Stockmayer⁶ has derived a distribution function describing the statistical heterogeneity under the assumption that the average copolymer composition remains constant during the copolymerization. Such assumption is fulfilled, for example, for azeotropic copolymerizations or for copolymerizations led to low conversions, when the conversion heterogeneity can be regarded as negligible.⁷ The equation

$$\sigma_s^2 = \frac{M_0}{M_n} \bar{w}(1 - \bar{w})\kappa \quad (3)$$

can then be derived for the variance of chemical composition due to the statistical heterogeneity σ_s^2 , where M_0 is the molecular weight of the monomeric unit (supposed to be the same for the two monomers), M_n is the number average molecular weight, and

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

where r_A and r_B are the copolymerization parameters of the monomers A and B. σ_s^2 reaches its largest value at $\bar{w} = 0.5$. This maximum, $\sigma_{s,\max}^2 = \Omega_s$, is given by the relation

$$\begin{aligned} \Omega_s(M_n) &= \frac{M_0 (r_A r_B)^{1/2}}{M_n \cdot 4} \quad \text{for } r_A r_B \geq \frac{1}{3} \\ \Omega_s(M_n) &= \frac{M_0 \sqrt{3}}{M_n \cdot 18(1 - r_A r_B)} \quad \text{for } r_A r_B \leq \frac{1}{3} \end{aligned} \quad (4)$$

Thus, Ω_s represents the upper limit of the statistical heterogeneity of a copolymer with a finite molecular weight for an infinitesimal weight conversion. For the majority of copolymers with molecular weights $M_n > 10^5$, it holds that $\Omega_s \lesssim 10^{-4}$.

The shape of the differential weight distribution function describing the conversion heterogeneity $g_c(w)$ can be derived for random copolymerization if the respective copolymerization parameters r_A and r_B and the ratio of monomer molecular weights, $t = M_{0A}/M_{0B}$, are known.⁸ For $r_A, r_B \neq 1$,

$$\begin{aligned} g_c(w) &= \left| \left(\frac{v}{v_0}\right)^{k_1} \left(\frac{v-1}{v_0-1}\right)^{k_2} \left(\frac{v-k_4}{v_0-k_4}\right)^{k_3} \left(\frac{k_1}{v} + \frac{k_2}{v-1} + \frac{k_3}{v-k_4}\right) \right. \\ &\quad \left. \times \frac{[v^2(r_B t + r_A - 1 - t) + v(1 + t - 2r_B t) + r_B t]^2}{v^2(r_A + r_B t^2 - 2r_A r_B t) + 2v t r_B (r_A - t) + r_B t^2} \right| \quad (5) \end{aligned}$$

where v_0 and v are compositions of the monomer mixture at the beginning and at a given moment of copolymerization, respectively, again given by the weight

fractions of monomer A. The parameters k_1 to k_4 are defined by

$$k_1 = \frac{r_B}{1 - r_B}, \quad k_2 = \frac{r_A}{1 - r_A},$$

$$k_3 = \frac{1 - r_A r_B}{(r_A - 1)(1 - r_B)}, \quad k_4 = \frac{t(1 - r_B)}{t(1 - r_B) + (1 - r_A)} \quad (6)$$

and the relation between w and v is determined by the copolymerization equation

$$w = \frac{v^2(r_A - t) + vt}{v^2[t(r_B - 1) + r_A - 1] + v(1 - 2r_B t + t) + r_B t} \quad (7)$$

It can be demonstrated that the distribution function $g_c(w)$ is identical with the true distribution function of chemical composition, $g(w)$, if the molecular weights of the copolymer chains approach infinity. Consequently, the function $g_c(w)$ can be regarded as a limiting form of the general function $g(w)$ corresponding to the state when the statistical heterogeneity can be neglected. Of course, if $g(w) = g_c(w)$, the variance of chemical composition due to conversion heterogeneity σ_c^2 equals the overall variance σ^2 .

Preliminary calculations show that σ_c^2 calculated according to eq. (1) using the function $g_c(w)$ mostly exceeds the values of σ_s^2 which corresponds to the statistical heterogeneity. Unlike statistical heterogeneity, conversion heterogeneity may be so high that it affects considerably the properties of the copolymers. For this reason, from here onward our attention is concentrated only on the conversion heterogeneity.

At a chosen initial composition of the monomer mixture, v_0 , the composition of the copolymer, w , formed in the given stage of copolymerization or the instantaneous composition of the monomer mixture, v , will be dependent on the weight conversion ψ . Thus, σ_c^2 is a function of five variables: r_A , r_B , t , v_0 , and ψ . For a particular monomer pair, the number of variables is reduced to two, namely, the initial composition of the monomer mixture, v_0 , and the weight conversion, ψ .

It is interesting to find the highest possible values of the heterogeneity parameter σ_c^2 which can be attained for a given pair of monomers at a given conversion, i.e., a quantity

$$\Omega_c(\psi) = \sup[\sigma_c^2(v_0, \psi)] \quad (8)$$

is sought, which in most cases is identical with one of the solutions to the equation

$$\left(\frac{\partial \sigma_c^2(v_0, \psi)}{\partial v_0} \right)_\psi = 0 \quad (9)$$

With respect to the involved form of the distribution function of chemical composition, $g_c(w)$, the integrals in eq. (1), and consequently the solution of eq. (9), must be determined numerically.

RESULTS AND DISCUSSION

Dependence of Heterogeneity Parameter σ_c^2 on Starting Composition of Monomer Mixture*Copolymerization Curves with Azeotropic Point*

If the copolymerization curve expressed by eq. (7) exhibits an azeotropic point, i.e., if both copolymerization parameters are either higher or lower than unity, it is possible to provide such copolymerization conditions under which the composition of the monomer mixture and of the forming copolymer will be identical. Under these conditions, the compositions of both the copolymer and the monomer mixture remain unchanged during the copolymerization, and the conversion heterogeneity of chemical composition is identically zero, independent of conversion.

The dependence of the parameter σ_c^2 on the initial composition of the monomer mixture, v_0 , for the copolymerization curve with the azeotropic point, or the dependence of $\log \sigma_c^2$ on v_0 , exhibits two local maxima [Figs. 1(a) and 1(b)], at least one of which meets condition (8). The higher the conversion, the higher usually is the heterogeneity of the product. An opposite case may also occur, however [Fig. 1(a)], if at higher conversions an almost pure homopolymer is formed. The resulting product is then mostly formed by this homopolymer and is consequently relatively chemically homogeneous compared to a lower conversion copolymer.

With respect to the shape of the distribution curves of chemical composition, systems should be discerned with both copolymerization parameters lower or higher than unity. In the first case ($r_A, r_B < 1$), at an appropriately chosen composition of the initial monomer mixture and at a sufficiently high conversion the composition of the forming copolymer may approach zero or unity, i.e., one of the homopolymers is formed (the other monomer is almost completely part of the copolymer and is virtually not at all contained in the monomer mixture). The differential distribution function of chemical composition may exhibit a minimum [Fig. 2(a)]. The resulting copolymerization product then resembles a mixture of a homopolymer and copolymer and also exhibits a high chemical heterogeneity.

If both copolymerization parameters are higher than unity ($r_A, r_B > 1$), then no similar case can arise. With increasing conversion the copolymer composition approaches the azeotropic composition [Fig. 2(b)]. The differential distribution functions of chemical composition always decrease monotonically toward the azeotropic composition. Monomeric systems of this type have been reported only exceptionally.

Copolymerization Curves without Azeotropic Point

If for the given monomer pair no azeotropic composition exists (i.e., if one of the copolymerization parameters is higher and the other lower than unity), then the dependence of $\log \sigma_c^2$ on v_0 at a given conversion exhibits a single maximum meeting condition (8) [Fig. 1(c)]. In principle, for the form of the distribution functions of chemical composition similar conclusions are valid as in the case

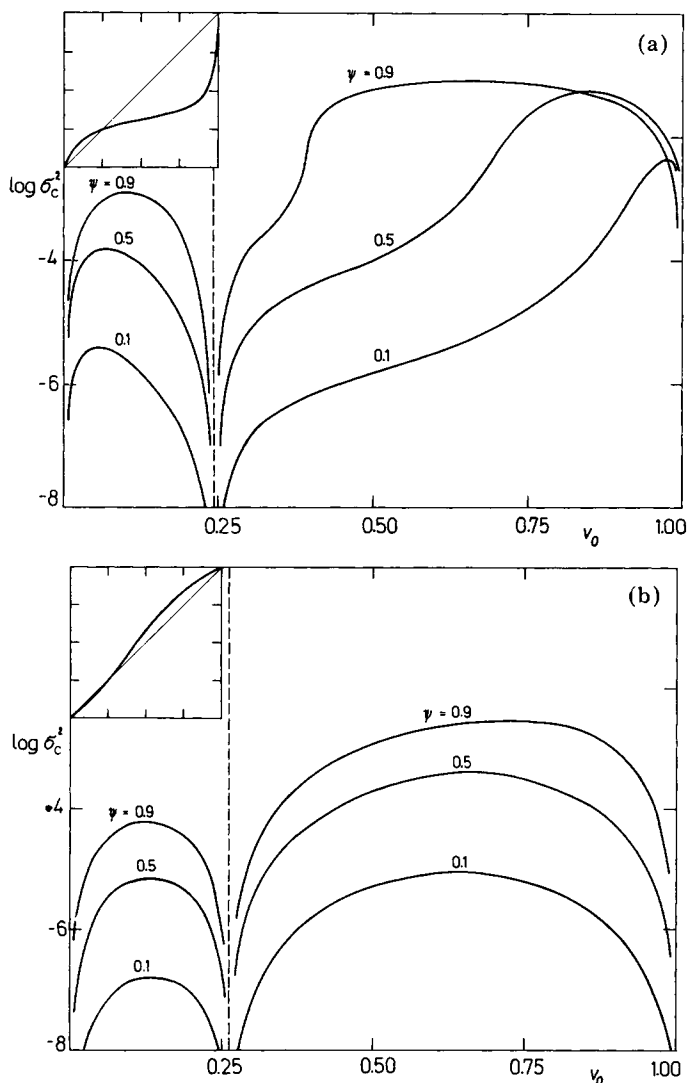


Fig. 1. Dependence of the logarithm of variance of the chemical composition, σ_c^2 , on the starting composition of the monomer mixture, v_0 , for various weight conversions ψ : (a) Acrylonitrile-styrene; $r_A = 0.04$, $r_B = 0.40$, $t = 0.51$. (b) Allyl benzoate-allyl chloride; $r_A = 2.50$, $r_B = 1.25$, $t = 2.13$. (c) Vinyl chloride-vinyl acetate; $r_A = 0.23$, $r_B = 1.68$, $t = 1.39$. (d) Acrylonitrile-isobutylene; $r_A = 1.02$, $r_B = 0$, $t = 0.95$. The composition v_0 is given by the weight fraction of the first monomer. Top left: copolymerization curve for the given comonomers. The copolymerization parameters taken from reference 15.

of both copolymerization parameters lower than unity [Fig. 2(c)]. If one of the copolymerization parameters is nil, the dependences of $\log \sigma_c^2$ on v_0 are defined only in a part of the interval (0, 1). This is explained by the fact that each time a composition of the initial monomer mixture, v_0 , can be found for which a monomer with a nonzero copolymerization parameter becomes entirely part of the copolymer, the copolymerization stops without reaching the required conversion [Fig. 1(d)].

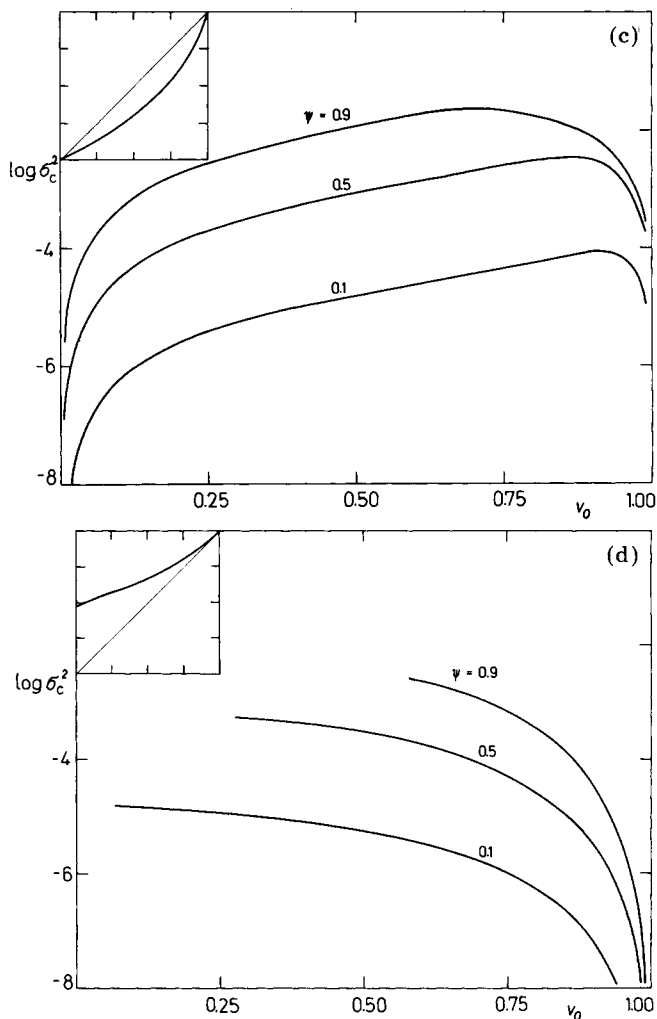


Fig. 1. (Continued from previous page)

Dependence of Highest Attainable Conversion Heterogeneity on Copolymerization Parameters

If the chosen pair of comonomers is copolymerized up to a weight conversion ψ , then for any initial composition of the monomer mixture, v_0 , the conversion heterogeneity of the product characterized by the parameter σ_c^2 will never exceed Ω_c . Thus, it holds that

$$\sigma_c^2 \leq \Omega_c \quad (10)$$

following definition (8) of the parameter Ω_c .

Figures 3(a)–3(c) show the parameter Ω_c for three different conversions and the molecular weight ratio of the monomers equal to unity. The curves were obtained by interpolating values of the parameter Ω_c calculated for pairs of the copolymerization parameters r_A and r_B , the values of which were varied by 0.1. A similar plot for the weight conversion $\psi = 0.9$, which is more interesting from the practical viewpoint and for which higher conversion heterogeneities of the

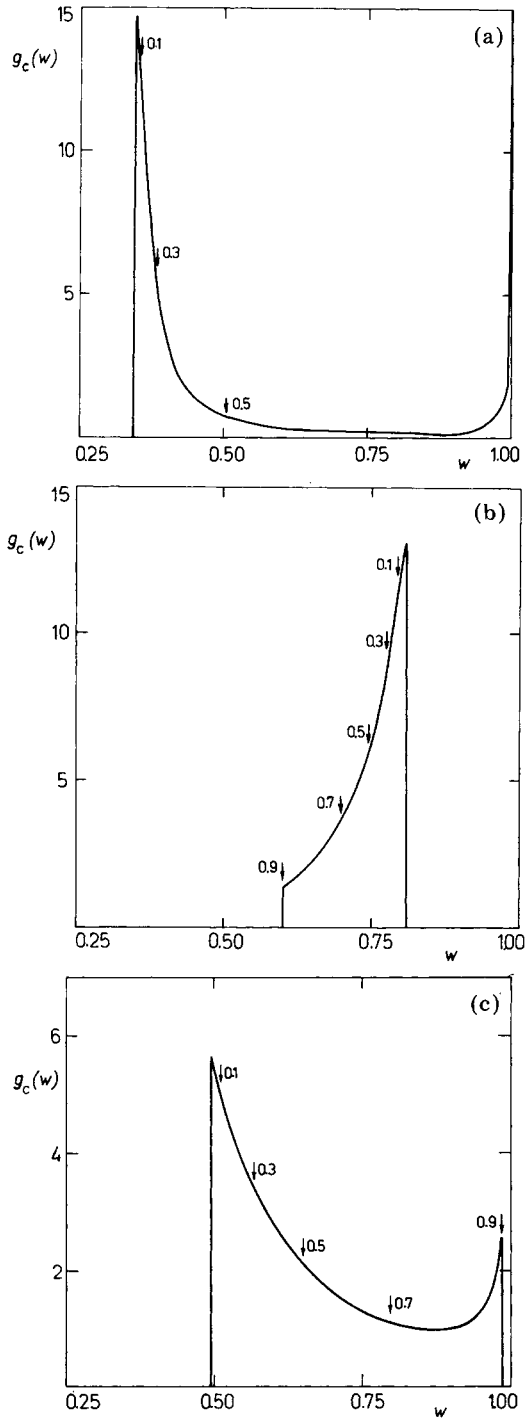


Fig. 2. Differential weight distribution function of chemical composition, $g_c(w)$, at the weight conversion $\psi = 0.9$. (a) Acrylonitrile-styrene; $\nu_0 = 0.66$. (b) Allyl benzoate-allyl chloride; $\nu_0 = 0.72$. (c) Vinyl acetate-vinyl chloride; $\nu_0 = 0.70$. Arrows indicate limits of the distribution function for conversions other than 0.9; at these conversions the shape of the section of the distribution function remains unchanged, but the function must be renormalized.

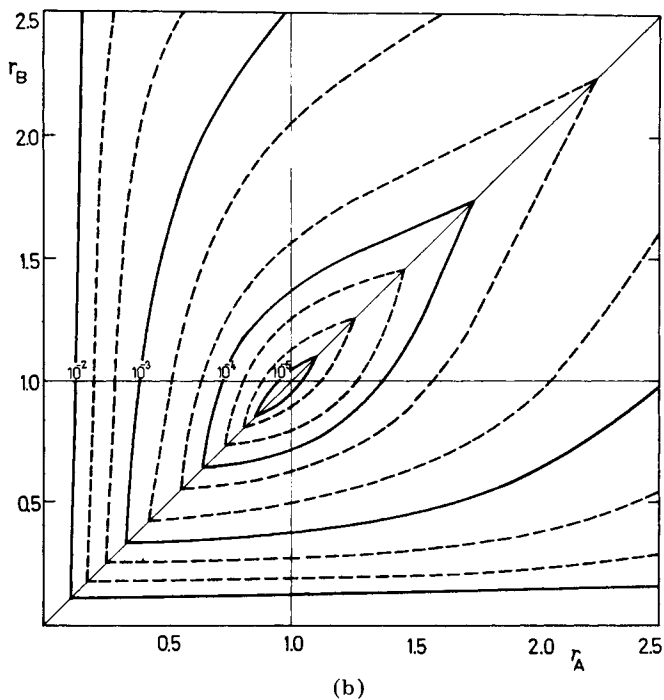
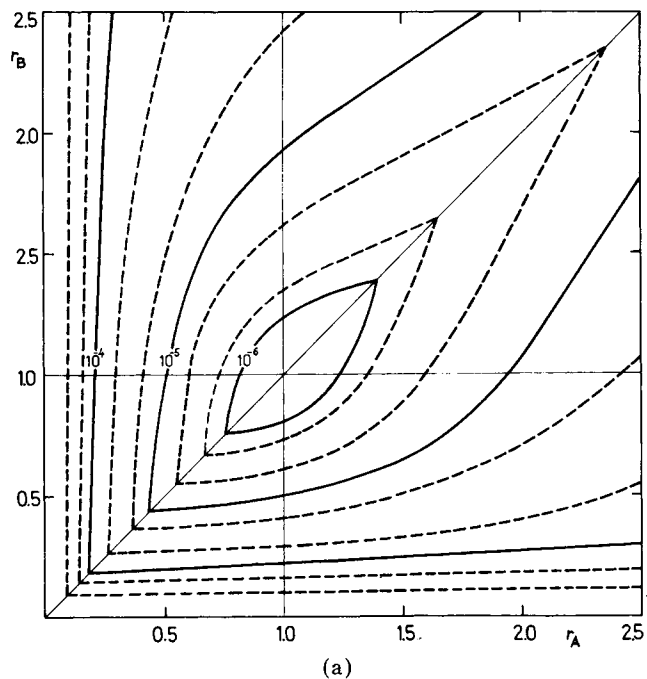


Fig. 3. Dependence of the maximum attainable value Ω_c of the conversion heterogeneity parameter σ_c^2 on the copolymerization parameters r_A and r_B at various weight conversions ψ . (a) $\psi = 0.1$; ratio of monomer molecular weights $M_{0A}/M_{0B} = t = 1$. (b) $\psi = 0.5$; $t = 1$. (c) $\psi = 0.9$; $t = 1$. (d) $\psi = 0.9$; $t = 2$. For $t = 0.5$, the axes r_A and r_B are to be mutually interchanged. Solid lines join Ω_c equal to integer powers of 10; dashed lines, their double and fivefold values.

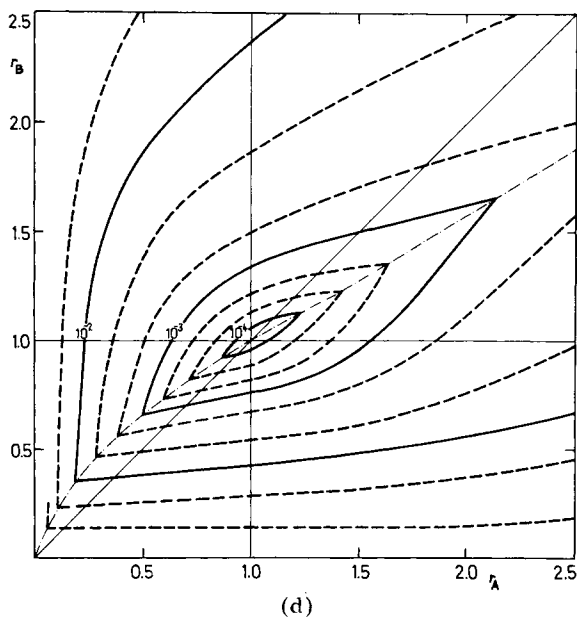
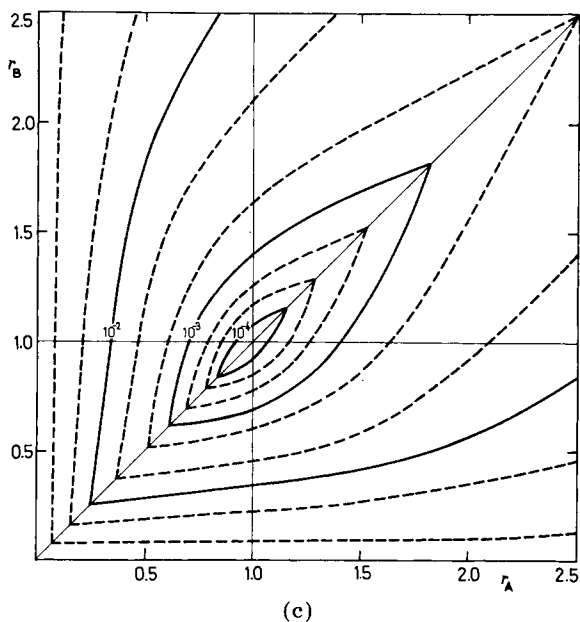


Fig. 3. (Continued from previous page.)

products can be expected, is given also for the molecular weight ratio of the monomers $t = 0.5$ and $t = 2$ [Fig. 3(d)] (monomer pairs with the parameters r_A, r_B, t and $r_B, r_A, 1/t$ are equivalent from the mathematical standpoint). Since the molecular weight ratio of the monomers for the majority of the monomer pairs lies within the interval (0.5, 2), the parameter Ω_c for a particular monomer pair can be estimated by interpolating data read off from Figures 3(c) and 3(d). By comparing these figures it can be seen that the molecular weight ratio of the

monomers, t , has a comparatively weak influence on Ω_c . As a rule, what we are interested in is not so much an exact value of Ω_c but rather its order of magnitude, which makes possible the upper estimate of the heterogeneity of a copolymer. Thus, the effect of the parameter t can be neglected to a considerable extent. For the sake of completeness, it should also be pointed out that if t is put equal to unity, the values of Ω_c represent the highest possible variance of chemical composition defined on the basis of molar fractions of monomers (irrespective of the actual value of t).

If both copolymerization parameters are smaller than unity, then the maximum attainable conversion heterogeneity is predominantly determined by the smaller one; the other copolymerization parameter has a less pronounced effect. This conclusion holds to some extent even if one of the copolymerization parameters is smaller than unity, while the other is larger. The more the copolymerization parameters differ from unity, the more increases Ω_c .

For an estimation of the maximum attainable overall chemical heterogeneity of copolymers with a finite molecular weight, for which generally $\sigma^2 \neq \sigma_c^2$, the following procedure is recommended: (1) From Figure 3, the maximum conversion heterogeneity Ω_c that can be attained by the copolymerization product is determined. Equation (4) is employed to estimate the statistical heterogeneity Ω_s . (2) If the statistical heterogeneity Ω_s can be neglected compared with the conversion heterogeneity Ω_c , the latter will determine the maximum overall chemical heterogeneity, and vice versa. (3) If the two types of chemical heterogeneity are comparable as to their magnitude, no unequivocal statement can be made regarding the overall chemical heterogeneity. An assumption seems justified, however, that in these cases the chemical heterogeneity will be so low as not to affect the properties of copolymers under investigation (see below).

Limiting Cases

Let us consider what values of the heterogeneity parameter Ω_c can be attained in limiting cases when both copolymerization parameters approach zero or infinity. If both copolymerization parameters equal zero, then the copolymerization product is a chemically homogeneous, strictly alternating copolymer, and the maximum chemical heterogeneity attainable in such a system is nil. On the other hand, Figure 3 shows that within the interval of the copolymerization parameters (0, 1), the maximum attainable conversion heterogeneity Ω_c increases monotonically along the straight line $r_A = r_B$ with decreasing copolymerization parameters. This is why the case is analyzed when the copolymerization parameters are not identically equal to zero but approach zero as a limit. Alternating copolymer is again the basic copolymerization product, but after one of the monomers has been exhausted, the copolymerization reaction need not stop but can continue giving rise to a homopolymer. A mixture of the alternating copolymer and one of the homopolymers results. It can be demonstrated (see Appendix) that the chemical heterogeneity of such a mixture will be highest for the same weight amounts of the alternating copolymer and homopolymer. A simple calculation yields

$$\begin{aligned} \lim_{r_A, r_B \rightarrow 0} \Omega_c &= \frac{1}{4} \left(\frac{t}{t+1} \right)^2 & \text{for } t \geq 1 \\ \lim_{r_A, r_B \rightarrow 0} \Omega_c &= \frac{1}{4} \left(\frac{1}{t+1} \right)^2 & \text{for } t \leq 1 \end{aligned} \quad (11)$$

At an arbitrary conversion of copolymerization, ψ , it is possible, by an appropriate choice of the initial composition of the monomeric mixture, ν_0 , to achieve each time a product consisting of a mixture of the same weight fractions of the copolymer and of one of the homopolymers. Thus, Ω_c is independent of conversion ψ .

The second limiting case, in which the two copolymerization parameters approach infinity, is hypothetical and does not occur in practice. The product of such a copolymerization would be a mixture of homopolymers. For both homopolymers present in the product in equal weight amounts, σ_c^2 assumes its absolute maximum, $\Omega_c = 0.25$.

Light Scattering and Chemical Heterogeneity

The chemical heterogeneity of copolymers can be characterized, for example, by the heterogeneity parameters P and Q , which for continuous distribution functions $f(w, M)$ are defined by⁹

$$P = \int_w \int_M M(w - \bar{w}) f(w, M) dM dw$$

$$Q = \int_w \int_M M(w - \bar{w})^2 f(w, M) dM dw$$
(12)

where \bar{w} is the average copolymer composition:

$$\bar{w} = \int_w \int_M w f(w, M) dM dw$$
(13)

Integration is carried out over the whole range of molecular weights and chemical composition for which $f(w, M)$ is nonzero. P and Q can be directly determined experimentally by measuring the apparent molecular weights M_{app} of copolymers in various solvents⁹:

$$M_{\text{app}} = M_w + 2P \left(\frac{\nu_A - \nu_B}{\nu} \right) + Q \left(\frac{\nu_A - \nu_B}{\nu} \right)^2$$
(14)

where ν , ν_A , and ν_B are the refractive index increments of the copolymer and of the constituent homopolymers in a given solvent. If the chemical composition and molecular weight distribution are independent of each other, it holds that $P = 0$, $Q = M_w \sigma^2$. Thus, under the above assumption, the parameter Q/M_w is identical with the variance σ^2 of the chemical composition of the copolymer.¹⁰

The applicability of light scattering and conditions under which the parameter Q/M_w can be determined with sufficient accuracy by this method has been discussed earlier.¹¹ Some estimated results, calculated assuming that the difference of the refractive index increment of homopolymers is 0.1 ml/g, can be briefly summarized as follows: (1) If Q/M_w is determined by light scattering measurement in one solvent (in which the refractive index increment of the copolymer is zero), then for $M_w = 10^6$, $Q/M_w > 0.025$ can be obtained with sufficient accuracy, and for $M_w = 10^5$, $Q/M_w > 0.22$. (2) If the parameter Q/M_w is to be determined by measurements in two solvents and if the experimental error is to be lower than 50%, then for $M_w = 10^6$ it must hold that $Q/M_w > 0.004$ and for $M_w = 10^5$, $Q/M_w > 0.037$. (3) Since in many real systems the experimental conditions are less favorable, the limit at which the application of light scattering

is still worth considering can in the first approximation be put at $Q/M_w = 0.01$. If the chemical heterogeneity of the copolymer is so low that $Q/M_w < 0.01$, then, with a few exceptions, this parameter cannot be determined by light scattering. In principle, the feasibility of light-scattering characterization of each particular copolymer has to be analyzed separately (see a few examples in Table I).

Thus, the determination of the heterogeneity parameters or proof of chemical heterogeneity of random copolymers by light scattering is practically not feasible if the copolymerization proceeds up to low conversions [cf. $\psi = 0.1$, Fig. 3(a)]. For high weight conversions, there already exists a range of copolymerization parameters where Ω_c can assume values higher than 0.01 [Figs. 3(c) and 3(d)]. This maximum value may, but by far need not, be reached in concrete copolymerization. Consequently, utilization of light scattering in the analysis of chemical heterogeneity of random copolymers is limited.

Fractionation of Chemically Heterogeneous Copolymers

Fractionation ranks among the most frequently used methods of detection and of a semiquantitative estimation of the chemical heterogeneity of copolymers. In a fractionation, the copolymer is separated into a number of fractions differing in solubility, and the isolated fractions are analyzed. The effectiveness of separation of copolymer molecules by their chemical composition in the fractionation greatly depends on the choice of the solvent system. When observing the effectiveness of fractionation by chemical composition, one must bear in mind the sensitivity of the analytical methods used in the determination of copolymer composition or its changes (e.g., elemental analysis, UV, IR, and NMR spectroscopy, differential refractometry, densitometry, etc.).

A hypothetical, chemically heterogeneous random copolymer with a rectangular distribution function of chemical composition having a width of 2 wt % monomer units is considered. With not too wide chemical composition distributions, a rectangular distribution is a good approximation of the real distribution. Such a copolymer, which has a corresponding heterogeneity parameter

TABLE I
Maximum Attainable Values of Variance of Chemical Composition Ω_c for Some Random Copolymers^a

Monomer	r_A	r_B	$10^2\Omega_c$	ν_0	$10^{-5}M_{w,\min}$
Acrylonitrile-butadiene	0.25	0.33	1.2	0.78	∞
Acrylonitrile-styrene	0.04	0.40	7.8	0.71	1
Acrylonitrile-vinyl chloride	3.28	0.02	16.3	0.70	∞
Butadiene-styrene	1.39	0.78	2.1	0.50	∞
Butadiene-vinyl chloride	8.80	0.04	13.3	0.48	4
Styrene-butyl methacrylate	0.63	0.64	0.1	0.77	∞
Styrene-ethyl methacrylate	0.67	0.26	1.2	0.28	3
Styrene-methyl methacrylate	0.50	0.50	0.2	0.21	∞
Vinyl acetate-vinyl chloride	0.23	1.68	2.2	0.68	7

^a r_A , r_B are copolymerization parameters; ν_0 is the initial composition of the monomer mixture (expressed by the weight fraction of monomer A) at which the variance of the chemical composition assumes its maximum at weight conversion $\psi = 0.9$. The chemical heterogeneity of samples synthesized under the specified conditions may be proved by light scattering¹¹ in at least two solvents if the molecular weight exceeds the estimate of $M_{w,\min}$. The copolymerization parameters refer to radical copolymerization at 60°C and were taken from ref. 15.

$\sigma^2 = 3.3 \times 10^{-5}$, is roughly the limiting case in which chemical heterogeneity can still be perceived with respect to fractionation effectiveness and to the sensitivity of the analytical methods. If the chemical composition distribution were essentially narrower, then even with an ideally effective fractionation by chemical composition the differences in the composition of fractions would lie within the limits of experimental error of the majority of common analytical methods. Phase separation methods have been reported allowing the separation of a mixture of two copolymers differing in the content of one of the components by 2 wt %.¹² The effectiveness of fractionation by chemical composition can—at least in principle—be further raised by refractionation or by crossfractionation.^{13,14} For this reason, sensitivity of the analytical methods must be regarded as the limiting factor. The heterogeneity parameter of an order of magnitude of 10^{-4} (under favorable circumstances up to 10^{-5}) may therefore be considered the limit of applicability of the phase separation methods, even if a highly effective fractionation procedure is available.

CONCLUSIONS

Calculations of the maximum attainable value Ω_c of the parameter of conversion heterogeneity σ_c^2 of random copolymers have shown that, if (a) copolymerization is carried out to low weight conversions ($\psi < 0.1$) and (b) the copolymerization parameters of the comonomers lie within the interval 0.2–2.5 (higher copolymerization parameters were not considered), the chemical heterogeneity of the copolymerization products can be proved neither by light scattering nor by fractionation. Within the limits of experimental error of the above methods, such copolymers can be regarded as chemically homogeneous.

For high conversion copolymerizations ($\psi > 0.9$), there exists a nonnegligible range of pairs of copolymerization parameters corresponding to monomers which may yield copolymers possessing a chemical heterogeneity perceptible by an appropriately performed fractionation and/or by light scattering. This heterogeneity may markedly, and mostly in an undesired manner, affect the results of light-scattering measurements (e.g., determination of the molecular weights of copolymers), or fractionations (e.g., in the preparation of samples of different molecular weights by the fractionation of a copolymer, the individual fractions may differ in chemical composition), and possibly also some properties of such copolymers.

At low conversion heterogeneities and low molecular weights, the overall heterogeneity can be seriously or even prevailingly affected by the statistical heterogeneity. But this is likely to happen at small overall heterogeneities which are not perceivable experimentally, anyway.

Appendix

Let us have a mixture of an alternating copolymer with one of the constituent homopolymers. Chemical composition of the alternating copolymer expressed as the weight fraction of the monomer units is given by

$$w_a = \frac{M_{0A}}{M_{0A} + M_{0B}} = \frac{t}{t + 1} \quad (\text{A1})$$

where t is the ratio of molecular weights of the monomer units M_{0A}/M_{0B} . The mixture of the alternating copolymer with the homopolymer A can be characterized by the average composition values

$$\bar{w} = W_a w_a + W_A, \quad \overline{w^2} = W_a w_a^2 + W_A \quad (\text{A2})$$

where W_a and W_A are the weight fractionations of the alternating copolymer and of the homopolymer A in the mixture. According to eq. (1), we obtain

$$\sigma^2 = (w_a - 1)^2 W_a (1 - W_a) \quad (\text{A3})$$

The maximum of σ^2 is looked for. The solution of the equation $d\sigma^2/dW_a = 0$ with respect to eq. (A1) yields

$$\sigma_{\max}^2 = \frac{1}{4} \left(\frac{1}{t+1} \right)^2 \quad \text{for } W_a = 0.5 \quad (\text{A4})$$

Similarly, for a mixture of the alternating copolymer with the homopolymer B, it can be derived as

$$\sigma_{\max}^2 = \frac{1}{4} \left(\frac{t}{t+1} \right)^2 \quad \text{for } W_a = 0.5 \quad (\text{A5})$$

Since

$$\left(\frac{t}{t+1} \right)^2 > \left(\frac{1}{t+1} \right)^2$$

for $t > 1$, the definition of Ω_c immediately gives relations introduced in the main text.

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