Graft Copolymer Statistics. 2. Application to Graft Copolymers Prepared from Macromonomers†

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ABSTRACT: Number and weight differential distribution functions of chemical composition have been derived for graft copolymers consisting of backbones with the most probable molecular-weight distribution and for grafts with the same molecular-weight distribution, or monodisperse grafts. The results describe products of random grafting and may be applied to copolymers prepared by the statistical copolymerization of a low-molecular-weight monomer and a macromonomer. Model calculations performed for copolymers containing 2 mol % of macromonomer units show that the distribution functions of chemical composition are relatively broad and that copolymer macromolecules may differ in the backbone content by as much as several tens weight percent. The distribution of chemical composition becomes narrower with increasing degree of polymerization of the backbone. Polydisperse macromonomer grafts provide a broader distribution of chemical composition of the copolymer compared with monodisperse grafts.

Introduction

In terms of the generally accepted IUPAC definition,[1,2] graft copolymers consist of macromolecules in which one or several blocks (grafts) are attached to the main polymer chain (backbone) as side chains, the grafts and backbone being derived from different monomers. Such a view of comblike macromolecules is adequately satisfied by graft copolymers prepared by statistical copolymerization of a low-molecular-weight monomer with a macromonomer.

A method much more often reported in the literature is random grafting of the existing backbones with grafts formed in situ by means of the radical polymerization of a vinyl monomer. The reason is the experimental simplicity of this method, compared with the preceding synthesis. However, such a procedure may lead to the formation of more complicated (e.g., cross-linked) structures, for instance due to the possibility of a radical recombination of two grafts propagating simultaneously from different backbones (H-type structures). Such structures do not completely satisfy the definition of a graft copolymer and are not considered in statistical models of graft copolymerization. This is one of the causes underlying difficulties involved in a comparison between experimental results and theoretical prediction.

A common feature of all the procedures for the preparation of graft copolymers described above is that the compounds thus obtained can be regarded as products of random grafting, even in those cases where the copolymer has been formed by statistical copolymerization of a monomer with a macromonomer. By analyzing the copolymerization equation, Rempp et al.[3,4] showed that if the molar content of the macromonomer in the copolymer is small (a few mole percent), then the distribution of both types of constitutional units in the copolymer main chain can be considered Bernouillian in the first approximation. The sequence arrangement of units in the copolymer chain (placement of the grafts) may then be regarded as independent of the reactivity ratios and is thus random.

Let us consider, for the purpose of illustration, that the copolymerization mixture contains 2 mol % of the macromonomer and that the monomer reactivity ratio of the latter is successively 0.2, 0.5, 1 (random process), and 2. Then, from simple sequence statistics,[5] we find that the corresponding number of isolated macromonomeric units (grafts) in the copolymer chain is 99.6, 99.0, 98.0 (random process), and 96.1%, and only the residual units participate in the formation of longer sequences, two-unit mostly, where the grafts are attached to the adjacent constitutional units of the backbone. Consequently, the sequence order of the chain does not differ much from random order, even though the reactivity ratio of the macromonomer assumes values quite far from unity (the sequence order of macromonomeric units virtually does not depend on the reactivity ratio of the second monomer[5]).

This study is concerned with a theoretical analysis of the chemical heterogeneity of randomly grafted copolymers and with the distributions of chemical composition of copolymer macromolecules. So far, no theoretical procedure that would predict or estimate, if only qualitatively, the chemical heterogeneity of graft copolymers prepared from a macromonomer has been reported in the literature. We shall restrict ourselves to binary copolymers, although, in principle, the theory could be extended to include multicomponent systems.[6]

In the case of statistical copolymers, and thus also graft copolymers prepared from a macromonomer, we meet with two types of chemical heterogeneity, namely, conversion[7] and statistical[8] heterogeneity. The source of conversion chemical heterogeneity consists in changes in the composition of the mixture of monomers, and thus also of the copolymer chains being formed with the conversion of copolymerization. This is a consequence of the usually different composition of the mixture of monomers and of the statistical copolymer thus formed. With copolymers prepared to low conversions this type of heterogeneity is negligible. At medium and high conversions its magnitude generally depends on the starting composition of the mixture of monomers and on the values of the reactivity ratios.[9] It is thought[4] that with copolymers prepared from a macromonomer this type of chemical heterogeneity should not become significant even at higher conversions. A conclusive answer might be provided by a theoretical analysis, which would respect the specific character of such a copolymerization, i.e., molecular weights of comonomeric units different by orders of magnitude.

Statistical heterogeneity originates in the statistical nature of formation of a copolymer chain.[8] For usual statistical copolymers its magnitude quickly decreases with

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increasing degree of polymerization,[8,10] and at the common degrees of polymerization (order of magnitude 10^3 and higher), it cannot be detected experimentally.[11,12] These conclusions are based on an assumption that the molecular weights of both comonomer units are comparable and they cannot therefore be applied mechanically to copolymers prepared from a macromonomer, where this condition is not fulfilled.

In this study, we examine the application of the statistics of random grafting to graft copolymers prepared by the statistical copolymerization of a macromonomer with a low-molecular-weight monomer. It is assumed that the molar content of macromonomeric units in the copolymer is small (units of mole percent). Below, we show that if backbones arising from this copolymerization have the most probable distribution of the degrees of polymerization (which may be assumed in many cases for radical copolymerization[13]), the distribution functions of chemical composition for the whole copolymer may be obtained in analytical form. Two cases are distinguished: (1) copolymer with monodisperse grafts, where all molecules of the macromonomer, and thus all the attached grafts, have the same molecular weight (statistical aspects of this case have not yet been reported in the literature); (2) copolymer with polydisperse grafts, when grafts, like the backbone, have the most probable molecular-weight distribution. This statistical model is a logical extension of our earlier considerations,[14,15] when the general Γ-distribution of molecular weights is reduced to the most probable distribution.

The two cases are discussed separately, because—as is shown below—the model of the copolymer with polydisperse grafts cannot simply be reduced to that with monodisperse grafts.

Theoretical Section

The following notation is used for the individual distribution functions: number functions are denoted with N; W is reserved for weight functions. Assignment of the distribution functions is specified by the subscript: A relates to the backbones, B relates to macromonomer grafts, and the functions related to macromolecules of the whole copolymer have no subscript. Letters in brackets before the vertical line denote the variable of the distribution function, and those after this line denote parameters of the function, which under other circumstances also appear as variables.

Monodisperse Grafts. The first case to be considered here is a graft copolymer prepared by the statistical copolymerization of a low-molecular-weight monomer A with a monodisperse macromonomer B. We assume that the backbones have the most probable number distribution of molecular weights, M_A

$$N_A(M_A) = \frac{1}{M_{nA}} \exp(-M_A/M_{nA}) \tag{1}$$

where M_{nA} is the number-average molecular weight of the backbones.

If we assume, moreover, that the molar content of the macromonomer is small, i.e., that macromonomer grafts are attached to the backbones randomly, then the probability that a backbone having the molecular weight M_A has m grafts attached to it may be approximated by the Poisson distribution[16]

$$N_A(m|M_A) = \frac{\lambda^m}{m!} \exp(-\lambda) \tag{2}$$

where[15] $\lambda = m_n M_A/M_{nA}$ and m_n is the average number of the attached grafts in one copolymer molecule.

The number fraction of backbones that have just m grafts attached, irrespective of the backbone molecular weight, is given by the integral[17]

$$N_A(m) = \int_{M_A} N_A(m|M_A) N_A(M_A)\, dM_A \tag{3}$$

which, after substitution from eq 1 and 2, gives a simple geometrical distribution

$$N_A(m) = (1 - r)^m r \tag{4}$$

The parameter r is defined by using the average number of grafts, m_n, by the relation

$$r = 1/(m_n + 1) \tag{5}$$

This parameter is often used below as the characteristic of the degree of grafting.

The number molecular-weight distribution of the backbones bearing m grafts, $N_A(M_A|m)$, may be derived from a general relation

$$N_A(M_A|m)N_A(m) = N_A(m|M_A)N_A(M_A) \tag{6}$$

After substitution from eq 1, 2, and 4, we obtain

$$\begin{aligned} N_A(M_A|m) &= \frac{1}{m!(rM_{nA})^{m+1}} M_A^m \exp\left(-\frac{M_A}{rM_{nA}}\right) \\ &= \Gamma(M_A;m+1,1/rM_{nA}) \end{aligned} \tag{7}$$

This distribution is of the Γ-type; for the variable z and the parameters a and b, it is defined, generally, as

$$\Gamma(z;a,b) = \frac{b^a}{\Gamma(a)} z^{a-1} \exp(-bz) \tag{8}$$

where $\Gamma(a)$ is the Γ-function of the parameter a, which for a positive integer a is $\Gamma(a) = (a - 1)!$ Since the average value of this distribution is a/b, e.g., the number-average molecular weight of backbones bearing m grafts is

$$M_{nA}(m) = (m + 1)rM_{nA} \tag{9}$$

For monodisperse grafts having the molecular weight M_B^*, the average molecular weight of the graft part is given by a simple multiple[18]

$$M_{nB}(m) = mM_B^* \tag{10}$$

In the following discussion, molecular weights or their averages for isolated grafts are denoted with an asterisk in order to distinguish them from the molecular weight of the whole graft part of the copolymer, which may be composed of a major number of grafts.

For whole copolymer macromolecules with m grafts we have[18]

$$M_n(m) = M_{nA}(m) + M_{nB}(m) \tag{11}$$

Relations 9–11 also hold in the case of polydisperse grafts discussed below, but for polydisperse grafts, M_B^* in eq 10 is replaced by the number-average M_{nB}^*.

At a given number of grafts, m, having a constant molecular weight, M_B^*, the molecular weight of the backbone, M_A, unambiguously defines the composition of the copolymer macromolecules, x, given by the weight fraction of its backbone part

$$x = M_A/(M_A + mM_B^*) \tag{12}$$

Here, the chemical composition, x, of a macromolecule with m grafts is a function only of the molecular weight of the backbone. If the grafts are polydisperse, backbones having a different molecular weight M_A may provide the same composition of a macromolecule with m grafts, when combined with grafts having a suitable molecular weight M_B^*.

This argument demonstrates that there are basic differences between the cases of monodisperse and polydisperse grafts; one consequence among many is that the relationships derived for polydisperse grafts do not reduce to those for monodisperse grafts when the limiting condition of an infinitely narrow molecular weight distribution is imposed. It is for this reason that the two cases are discussed separately.

If the molecular-weight distribution of backbones in copolymer macromolecules with m grafts attached to them is known (eq 7), it is possible to calculate the number distribution function of chemical composition of these macromolecules, because it is known that

$$N(x|m) = N_A(M_A|m)\frac{dM_A}{dx} \tag{13}$$

Equation 13 ensues from a general relation between the distribution of a random quantity and the distribution of a function of that quantity. The weight distribution function is obtained from the relation

$$W(x|m) = \frac{M_A + mM_B^*}{M_n(m)}N(x|m) \tag{14}$$

which is a general relation between the number and weight distribution.

After substitution from eq 7 and 12 and a rearrangement, we obtain the number and weight distribution function of chemical composition in the form

$$N(x|m)\,dx = \frac{(mQ)^m}{(m-1)!}\exp(-mQ)\,dQ \tag{15}$$

$$W(x|m)\,dx = \frac{1-x_w(m)}{1-x}\frac{[m(1-r)Q\exp(-Q)]^m}{(m-1)!}\,dQ \tag{16}$$

where we have denoted

$$Q = \frac{1}{1-r}\frac{1-x_w}{x_w}\frac{x}{1-x} \tag{17}$$

and where the average composition of the assembly of macromolecules bearing m grafts is given by[18]

$$x_w(m) = \frac{M_{nA}(m)}{M_n(m)} = \left[1 + \frac{m}{m+1}\frac{1-x_w}{x_w}\frac{1}{1-r}\right]^{-1} \tag{18}$$

as ensues from eq 9–11; finally, the average composition of the whole copolymer is defined as[18]

$$x_w = M_{nA}/M_n \tag{19}$$

where M_n is the number average of its molecular weight. Using the definition of the Γ-distribution, one may also write eq 15 as

$$N(x|m)\,dx = \Gamma(Q;m+1,m)\,dQ \tag{20}$$

The distribution functions of chemical composition in the whole "true" copolymer (i.e., excluding the ungrafted backbones; this condition is recalled below by a cross in the superscript of the distribution functions) are obtained by the weighted sum

$$N^+(x) = \frac{1}{1-N(0)}\sum_{m=1}^{\infty}N(x|m)N(m) \tag{21}$$

$$W^+(x) = \frac{1}{1-W(0)}\sum_{m=1}^{\infty}W(x|m)W(m) \tag{22}$$

where $N(m)$ and $W(m)$ are the number and weight fractions of macromolecules containing m grafts. Since the number of macromolecules containing m grafts is the same as that of backbones bearing m grafts

$$N(m) = N_A(m) \tag{23}$$

and $N_A(m)$ is given by eq 4; the weight distribution

$$W(m) = \frac{M_n(m)}{M_n}N(m) = \left[m\frac{1-x_w r}{1-r} + x_w\right](1-r)^m r^2 \tag{24}$$

is determined from eq 11, 19, and 23. $N(0) = r$ and $W(0) = r^2x_w$ are the number and weight fraction of macromolecules, respectively, which contain no grafts, as ensues from eq 23 and 24 after the substitution $m = 0$.

Equations 21 and 22 then yield, respectively, the resulting number and weight differential distribution functions of chemical composition of macromolecules in the "true" graft copolymer in the form of series

$$N^+(x)\,dx = \frac{r}{1-r}\sum_{m=1}^{\infty}m\frac{[m(1-r)Q\exp(-Q)]^m}{m!}\,dQ \tag{25}$$

$$W^+(x)\,dx = \frac{r^2x_w}{1-r^2x_w}\frac{Q}{x}\sum_{m=1}^{\infty}m^2\frac{[m(1-r)Q\exp(-Q)]^m}{m!}\,dQ \tag{26}$$

For values $r \ll 1$, i.e., for high degrees of grafting (cf. eq 5), both series converge in the neighborhood of the maximum of the distribution function only very slowly, which makes their application in practical calculations difficult. The use of Stirling's approximation yields

$$m! = m^m[\exp(-m)](2\pi m)^{1/2} \tag{27}$$

which for $m \gtrsim 20$ simplifies the terms of series 25 and 26.

Polydisperse Grafts. A general case of random grafting of polydisperse backbones with polydisperse grafts, assuming that both assemblies obey the Schulz–Zimm (Γ) molecular-weight distribution, has been discussed in earlier papers.[14,15] If we assume that both the backbones and the grafts have the most probable molecular-weight distribution, then the reported general relations may be simplified for the examined case by substituting $y_A = m + 1$, $y_B = m$ in ref 14, and by $y_A = y_B = 1$ in ref 15.

On this assumption, eq 30 and 31 in ref 14 and eq 29 in ref 15, which give expressions for the number and weight distribution functions of chemical distribution of copolymer macromolecules bearing m grafts, may be rewritten as

$$N(x|m) = \frac{h_A + h_B}{h_A h_B}[h_A x + h_B(1-x)]W(x|m) \tag{28}$$

$$W(x|m) = \frac{(h_A+q)^{m+2}h_B^{m+1}}{(m+1)h_B + m(h_A+q)}\frac{\Gamma(2m+2)}{\Gamma(m+1)\Gamma(m)} \times \frac{x^m(1-x)^{m-1}}{[(h_A+q)x + h_B(1-x)]^{2m+2}} \tag{29}$$

where $h_A = 1/M_{nA}$, $h_B = 1/M_{nB}^*$, and $h_A + q = 1/rM_{nA}$; M_{nB}^* is the number-average molecular weight of the individual grafts, and, according to eq 9, rM_{nA} is the number-average molecular weight of residual ungrafted backbones.

After replacement of the parameters h_A, h_B, and $h_A + q$ by the parameters r and x_w, used in the discussion of the preceding case of monodisperse grafts, eq 28 and 29 can be rewritten as

$$N(x|m)\,dx = \frac{(2m)!}{m!(m-1)!}\frac{Q^m}{(1+Q)^{2m+1}}\,dQ \tag{30}$$

$$W(x|m)\,dx = \frac{1 - x_w(m)}{1 - x}\,\frac{(2m+1)!}{(m!)^2}\,\frac{Q^m}{(1+Q)^{2m+2}}\,dQ \quad (31)$$

The meaning of the other symbols is the same as in eq 15 and 16. Equations 30 and 31 can be rewritten in a more compact form (less suitable for calculation) by introducing the substitution $z = Q/(1 + Q)$

$$N(x|m)\,dx = \mathrm{B}(z;m+1,m)\,dz \quad (32)$$

$$W(x|m)\,dx = [x_w(m)\mathrm{B}(z;m+2,m) + (1 - x_w(m))\mathrm{B}(z;m+1,m+1)]\,dz \quad (33)$$

where the B distribution of the variable z with the parameters a and b is generally defined as

$$\mathrm{B}(z;a,b) = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} z^{a-1}(1-z)^{b-1} \quad (34)$$

Similarly to the preceding case of monodisperse grafts, the number and weight distribution functions of chemical composition in the "true" copolymer can be obtained by using eq 21–24, which hold both for monodisperse and for polydisperse grafts. Summation prescribed by eq 21 and 22 gives the final result

$$N^+(x)\,dx = \frac{2rQ}{[(1-Q)^2 + 4rQ]^{3/2}}\,dQ \quad (35)$$

$$W^+(x)\,dx = \frac{r^2x_w}{1 - r^2x_w}\,\frac{1-r}{x}\,\frac{6Q^2(1+Q)}{[(1-Q)^2 + 4rQ]^{5/2}}\,dQ \quad (36)$$

By numerical analysis, it can be demonstrated that some less common summations used in deriving eq 35 and 36 may be presented in the form

$$\sum_{m=1}^{\infty} \frac{(2m+1)!}{(m!)^2} X^m = \frac{1}{(1-4X)^{3/2}} \quad (37)$$

$$\sum_{m=1}^{\infty} \frac{(2m+1)!}{m!(m-1)!} X^m = \frac{6X}{(1-4X)^{5/2}} \quad (38)$$

Discussion

All the distribution functions of chemical composition presented in the Theoretical Section, especially by eq 25, 26, 35, and 36, depend only on two experimentally accessible parameters. The first parameter is the average chemical composition of the copolymer, x_w (given by the weight fraction of backbones in the copolymer), and the other is the grafting parameter r, which is simply related to the average number of grafts, m_n, by definition 5. In practice, the average number of grafts in the given copolymer, and thus also the parameter r, may be calculated from

$$m_n = F_B P_{nA} \quad (39)$$

where F_B is the mole fraction of the macromonomer (grafts) in the graft copolymer and P_{nA} is the number-average degree of polymerization of the backbone (which may not be known). Another route, if the number-average molecular weights of the macromonomer, M_{nB}*, and of the whole copolymer, M_n, are available, is the calculation using the relation

$$m_n = \frac{(1 - x_w)M_n}{M_{nB}^*} \quad (40)$$

where the numerator is the number-average molecular weight of the whole graft part of the copolymer.[18]

Let this be illustrated by statistical copolymerization of a low-molecular-weight monomer having the molecular weight $M_{0A} = 100$ with a macromonomer having the most probable molecular-weight distribution (polydisperse case) and the number-average molecular weight $M_{nB}^* = 20\,000$. Let copolymer chains contain, e.g., 2 mol % (=80 wt %) of macromonomeric units ($F_B = 0.02$) on the average; then, one graft is attached, on the average, to each 50th constitutional backbone unit. Let us now compare how the distribution of chemical composition of the individual copolymer macromolecules depends on the number-average molecular weight of the backbone M_{nA}, if in all cases the average copolymer composition, i.e., the macromonomer content, remains unchanged ($x_w = 0.2$). If we choose the successive molecular weights of the backbone $M_{nA} = 5 \times 10^3$, 5×10^4, 2×10^5, and 5×10^5, then the other parameters of the graft copolymer assume values given in Table I. At higher degrees of grafting ($m_n > 10$), the weight fraction of ungrafted backbones in the copolymer, $W(0) = r^2x_w$, is very small (Table I). In practice, this means

Table I
Parameters of Model Graft Copolymers Having Backbones of Various Molecular Weight M_{nA} ($M_{0A} = 100$) and Macromonomer Grafts ($M_{nB}^* = 20\,000$), the Mole Fraction of Which in the Copolymer Is Always $F_B = 0.02$ ($x_w = 0.2$)[a]

example	$10^{-3}M_{nA}$	m_n	r	$10^{-3}M_n$	x_w^+	$W(0)$
1	5	1	0.5	25	0.158	5×10^{-2}
2	50	10	0.1	250	0.198	2×10^{-3}
3	200	40	0.025	1000	0.200	1.25×10^{-4}
4	500	100	0.01	2500	0.200	2×10^{-5}

[a] $m_n = F_B M_{nA}/M_{0A}$ is the mean number of attached grafts, $r = (m_n + 1)^{-1}$ is the parameter of grafting, $M_n = M_{nA} + m_n M_{nB}^*$ is the number-average molecular weight of the whole copolymer, and $x_w^+ = (x_w - W(0))/(1 - W(0))$ is the average chemical composition of a true graft copolymer formed after the separation of ungrafted backbones, the weight fraction of which in the copolymer is $W(0) = r^2x_w$.

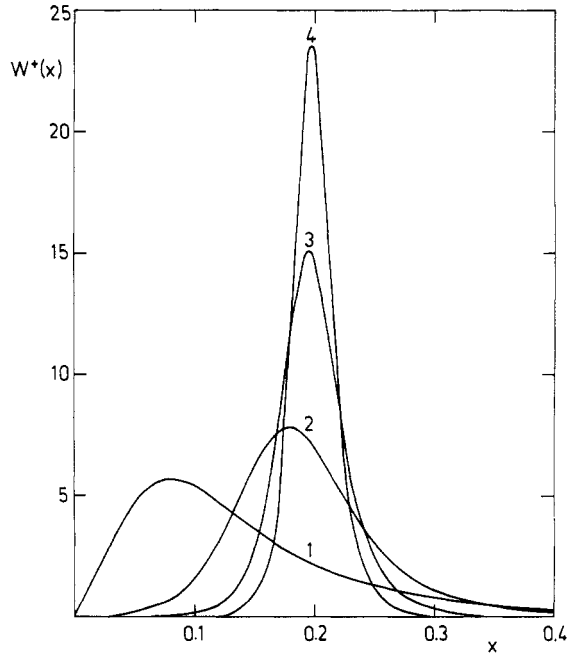

Figure 1. Differential weight distribution function, $W^+(x)$, of chemical composition, x, of true graft copolymers prepared by the statistical copolymerization of a low-molecular-weight monomer having the molecular weight $M_{0A} = 100$ with a polydisperse macromonomer having the number-average molecular weight $M_{nB}^* = 20\,000$. Copolymers, including ungrafted backbones, contain 2 mol % (=80 wt %) of macromonomer grafts (average composition expressed by the weight fraction of the backbone is $x_w = 0.2$) and differ in the molecular weight of the backbone, $M_{nA} = 5000$ (curve 1), 50 000 (2), 200 000 (3), and 500 000 (4). Cf. also Table I.

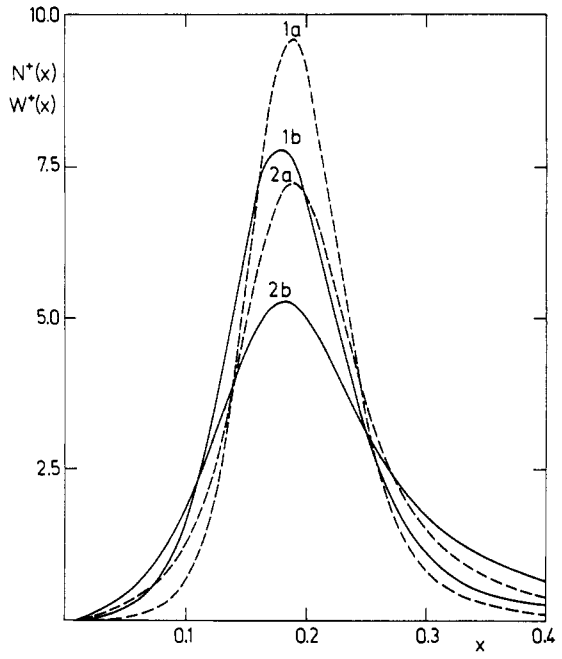

Figure 2. Comparison between the differential weight distribution functions of chemical composition, $W^+(x)$ (curves 1), and number functions, $N^+(x)$ (curves 2), for a model graft copolymer with monodisperse grafts (curves a, broken) or polydisperse grafts (curves b, solid). Parameters of the graft copolymer correspond to example 2 in Table I and Figure 1.

that under such conditions there is no need to distinguish formally between the graft copolymer, which contains ungrafted backbones, and the true graft copolymer, which is formed after their separation. In those cases where the attached number of grafts is small (example 1), this differentiation is called for.

The differential weight distribution functions of chemical composition of true graft copolymers are relatively broad (Figure 1) and become narrower and more symmetrical, as expected, with increasing degree of grafting. The displacement of the distribution function for the least grafted copolymer (curve 1, Figure 1) toward lower composition values is related to the lower average content of the backbones, x_w^+, in this copolymer. These distribution functions describe the statistical chemical heterogeneity of graft copolymers, i.e., differences in the chemical composition of the individual copolymer macromolecules which originate in their statistical (or random, in this case) formation. The role played by the so-called conversion chemical heterogeneity would bring about further broadening of the distribution functions.[10]

Figure 2 presents a comparison between the number and weight distribution functions of chemical composition for monodisperse and polydisperse grafts. Unlike the weight distribution functions, the number distribution functions are not experimentally available, and therefore they are given here only for the sake of illustration. As expected, both types of distribution functions of copolymers with monodisperse grafts are narrower than in the case of polydisperse grafts. The character of the distribution functions is similar in both cases, and it may be assumed that the effect of polydispersity of grafts on the distribution of chemical composition of the copolymer is weak.

Compared with the statistical chemical heterogeneity of copolymers arising by the classical copolymerization of two low-molecular-weight monomers,[8,10] the distributions of chemical composition of graft copolymers prepared from the macromonomer are, at equal weight composition, much broader. With a suitably chosen and efficient fractionation method, the chemical heterogeneity of such copolymers should be experimentally detectable.

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