Graft Copolymer Statistics†

Jaroslav Stejskal,* Jitka Horská, and Pavel Kratochvíl

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received July 20, 1983*

ABSTRACT: We analyze a model of graft copolymer, assuming that (a) grafts are attached to the backbone randomly, (b) copolymer macromolecules consist of one backbone and simple grafts, and (c) molecular weights of both the parent and attendant homopolymer molecules obey the Schulz-Zimm distribution. The distribution of backbones into the individual copolymer species (i.e., sets of macromolecules with a given number of attached grafts), the distribution of the occurrence of these species, and the distribution of their molecular weights and chemical composition are presented. Calculation of the distribution of chemical composition of the whole graft copolymer is demonstrated. All data concerning the copolymer and its parts and components in the given model can be expressed by means of experimentally available quantities, viz., molecular weights of the parent and attendant homopolymer and of a quantity characterizing the degree of grafting (chemical composition of the copolymer, weight fraction of ungrafted backbones, etc.). Quantities calculated by model concepts are compared with experimentally determined characteristics of polystyrene-*g*-poly(methyl methacrylate) prepared by a radical graft reaction.

The formation of a graft copolymer can be described by a specific statistical model[1-5] which more or less reflects the physical reality. It is appropriate to express the results of model calculations in terms of experimentally available quantities. This enables us to verify the suitability of the model for a particular type of the copolymer. To characterize the grafting process, the following data should be known or should be assumed to be known:

(a) Characteristics of the initial set of backbones and grafts which, if combined, can model formation of the copolymer. Usually, four parameters are sufficient, namely, weight- and number-average molecular weights of the original backbones, M^*_{nA} and M^*_{wA}, and of the grafts, M^*_{nB} and M^*_{wB}. In some cases it is suitable, or necessary, to assume a certain type of molecular weight distribution.

(b) Extent of grafting, i.e., a measure of the number of grafts attached to the backbones. This extent is determined by, e.g., chemical composition of the copolymer, x_w, weight fraction of ungrafted backbones, molecular weights of the graft or backbone part of the copolymer and of the copolymer as a whole, and the like.

If characteristics of the initial sets of backbones and grafts are known, it is possible, in principle, to calculate all the remaining quantities from any quantity which depends on the extent of grafting. The agreement or variance between experimental data and values thus calculated may serve as a criterion of the validity of the model by which the mutual relation between the individual quantities is prescribed or may be used to evaluate the potential of the method of experimental characterization of a graft copolymer.

From the statistical viewpoint, the description of a graft copolymer is identical, in principle, with that of comblike macromolecules. The latter has been adequately worked out for the characterization of branching,[6] and some results may be applied directly to graft copolymers. It seems therefore surprising that, in the overwhelming majority of cases, the graft copolymers and comblike homopolymers are dealt with separately in the literature. For graft copolymer macromolecules, only one additional factor appears, namely, the different chemical nature of the backbone and of the attached grafts. Our attention has thus been concentrated predominantly on the description of the chemical composition of the individual copolymer macromolecules and on the distribution of chemical composition in the whole copolymer.

At present, there is a large number of papers dealing with the preparation of graft copolymers; in particular, application of grafting in the modification of properties of industrial and natural polymers is widely used.

A theoretical description of grafting, even if based on simplifying model assumptions, appears only sporadically, and some of the literature sources are not readily available. The subsequent theoretical part of this paper is based on information contained in the literature, which is summarized by using unified symbolics, critically evaluated, and supplemented in many instances. It has been regarded as useful to classify the existing knowledge in order to point out the generation of the results which ensue from model conceptions. At the same time, emphasis was laid on the possibility of comparing the results thus obtained with the experimental ones. An attempt to do so has been made using polystyrene-*g*-poly(methyl methacrylate) copolymers as an example.

Theoretical Section

Model of Graft Copolymer. The graft copolymer is a mixture of macromolecules consisting of a block of constitutional units of type A (backbone) having blocks of units of type B (grafts) attached to them (Figure 1). In addition to the genuine copolymer macromolecules, the "rough copolymer product" usually contains ungrafted backbones and also, according to the conditions of preparation, the attendant graft homopolymer. The part of the graft copolymer which consists of macromolecules bearing grafts attached to the backbone will be referred to as the "true copolymer". If the "graft copolymer" is mentioned, this always means the true copolymer containing moreover ungrafted backbones (i.e., homopolymer A). Such copolymer would be a product of an ideal grafting reaction in which the attendant graft homopolymer B would not form.

Copolymer macromolecules can be divided into groups depending on how many attached grafts they contain. The set of all copolymer macromolecules consisting of a single backbone with a given number of grafts attached is called a "copolymer species".

The following assumptions are made about the formation of the graft copolymer:

(a) Attachment of grafts to backbones is random.[1-5] Each segment of the backbone has the same probability to be grafted. By "segment" we understand here a part of the backbone to which just one graft can be attached.[2]

† We are happy to have the opportunity of dedicating this paper to Professor Walter H. Stockmayer, a paragon of scientist and man, on the occasion of his 70th birthday.

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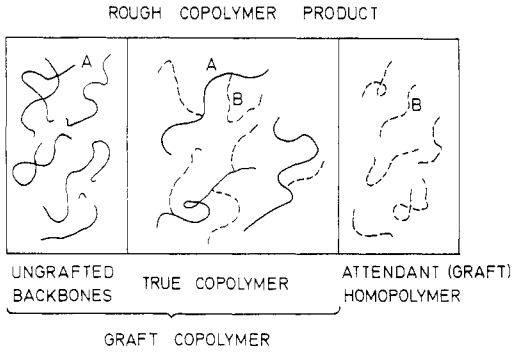

Figure 1. Components of the rough copolymer product.

Probability of attachment of another graft to the backbone is not affected by the grafts already attached to it.[1,3,4]

(b) Copolymer macromolecules are composed of a single backbone having simple grafts attached to it; i.e., macromolecules are of the comblike type. No further grafting of grafts (formation of branched grafts) is contemplated.[4] The molecular weight distribution of the backbones (both grafted and ungrafted) remains unchanged during the copolymerization;[3] i.e., the backbones neither cross-link nor degrade.

(c) The molecular weight distribution of homopolymer A which is grafted (also called substrate, parent, or mother polymer) and of the set of chains of type B which would form by tearing off the attached grafts (this set is identified with the attendant graft homopolymer or is related to the latter in a simple manner) can be approximated by the Schulz–Zimm (Γ) distribution. From here onward, molecular weights and molecular weight distribution functions of these homopolymers are denoted with an asterisk. Let the number distribution of molecular weight M^*_K be described by the relation

$$N^*_K(M^*_K) = \Gamma(M^*_K; y_K, h_K) = \frac{h_K{}^{y_K}}{\Gamma(y_K)} M^*_K{}^{y_K-1} \exp(-h_K M^*_K) \quad (1)$$

where K = A or B and y_K and h_K are positive parameters related to the average molecular weights by

$$y_K = (M^*_{wK}/M^*_{nK} - 1)^{-1}$$
$$h_K = (M^*_{wK} - M^*_{nK})^{-1} \quad (2)$$

The former parameter is a measure of the width of the molecular weight distribution, and the latter is related with its position.

Thus, in total we need five input data, which are assumed to be known: (a) molecular weight averages of the parent homopolymer M^*_{nA} and M^*_{wA}, or the corresponding parameters y_A and h_A; (b) molecular weight averages of the set of grafts (attendant homopolymer), M^*_{nB} and M^*_{wB}, or the respective parameters y_B and h_B; and (c) the chemical composition of the copolymer x_w (or another quantity related to the extent of grafting, e.g., the grafting parameter q defined below).

Then it is possible to (a) statistically describe characteristics of the individual copolymer species (i.e., sets of macromolecules with the given number of attached grafts), (b) determine the share of the individual copolymer species in the copolymer, and (c) characterize the whole graft copolymer by weighted averages of characteristics of the copolymer species which form the given copolymer.

Distribution of Backbones and Copolymer Species in the Graft Copolymer. (a) Backbones. An expression for the probability that just m grafts are attached to the backbone, if its molecular weight is M_A, for general comblike macromolecules has been reported by Orofino[6] and for graft copolymers independently by several other authors.[1-4] The corresponding distribution function is given by a binomial distribution

$$N_A(m|M_A) = b(m; n, p) = \binom{n}{p} p^m (1-p)^{n-m} \quad (3)$$

This distribution function, denoted here as conditional, gives the number fraction of backbones (of the set of all backbones having the molecular weight M_A) which carry just m grafts. At the same time, it equals the weight fraction of backbones of the species,[3] $W_A(m|M_A)$, because the set of backbones the molecular weight of which is just M_A is monodisperse by virtue of definition. The parameter p is the probability that a polymer segment has been grafted and n is the total number of segments of the backbone. A parameter

$$q = np/M_A$$

is suitably introduced, representing the probability that a randomly chosen segment of the backbone has been grafted, related to the unit molecular weight of the segment, $M_A{}^0 = M_A/n$. In the case that each repeating constitutional unit of the backbone has the same probability of being grafted, the segment can be identified with such a unit. The parameter q is related to a number of experimentally available quantities. It characterizes the extent of grafting and is, in principle, analogous to the branching index λ (number of trifunctional sites per unit molecular weight of a branched macromolecule) introduced by Zimm and Stockmayer.[7]

For a low degree of grafting, where $m \ll n$, the binomial distribution (3) can be approximated by the Poisson distribution[2] with a single parameter qM_A

$$N_A(m|M_A) = p(m; qM_A) = \frac{(qM_A)^m}{m!} \exp(-qM_A) \quad (4)$$

The approximation is not suited for graft copolymers approaching the starlike structure, because here the condition $m \ll n$ is usually not fulfilled.

For a two-dimensional distribution function $N_A(m,M_A)$ the relation

$$N_A(m,M_A) = N_A(m|M_A)N_A(M_A) = N_A(M_A|m)N_A(m) \quad (5)$$

holds. The number fraction of backbones carrying just m grafts, $N_A(m)$, independently of their molecular weight, is obtained by integrating the two-dimensional distribution function (5) over all molecular weights of backbones. The molecular weight distribution of backbones in the copolymer, $N_A(M_A)$, is identical with that of the substrate, $N^*_A(M^*_A)$, given by the Γ-distribution (1). The integration

$$N_A(m) = \int_{M_A} p(m; qM_A)\Gamma(M_A; y_A, h_A)\, dM_A \quad (6)$$

yields the number distribution of backbones carrying just m grafts[4] as a negative binomial (Pascal) distribution[9]

$$N_A(m) = n(m; y_A, r) = \frac{\Gamma(y_A + m)}{\Gamma(y_A)m!}(1-r)^m r^{y_A} \quad (7)$$

with two positive parameters, y_A and $r = h_A/(h_A + q)$. The parameter r has the meaning of the ratio between the number-average molecular weight of ungrafted backbones in the copolymer and that of the starting parent polymer, $M_{nA}(0)/M^*_{nA}$, as ensues for eq 2 and 18. The weight fraction, $W_A(m)$, is also given by this type of distribution[8,9]

$$W_A(m) = \frac{M_{nA}(m)}{M_{nA}} N_A(m) = n(m; y_A + 1, r) \quad (8)$$

where the number-average molecular weight of backbones in copolymer macromolecules carrying m grafts, $M_{nA}(m)$, is given by eq 18, to be derived later.

The distribution functions given so far depend on three parameters only, viz., y_A, h_A, and q. The former two are available from eq 2 after determining the number- and weight-average molecular weights of the parent polymer, M^*_{nA} and M^*_{wA}. The parameter q which describes the extent of grafting can, e.g., be evaluated from the experimentally determined weight fraction of ungrafted backbones

$$W_A(0) = \left(\frac{h_A}{h_A + q}\right)^{y_A+1} \tag{9}$$

as ensues from eq 8 after substitution $m = 0$ or from the chemical composition of the copolymer according to eq 28.

(b) Copolymer Species. The number of macromolecules containing m grafts is identical with that of backbones carrying m grafts; therefore, the number fraction of copolymer macromolecules having m grafts is

$$N(m) = N_A(m) = n(m; y_A, r) \tag{10}$$

In its general form, the weight fraction of these macromolecules is given by

$$W(m) = \frac{M_n(m)}{M_n} N(m) \tag{11}$$

where the number-average molecular weight of the given copolymer species, $M_n(m)$, and of the whole copolymer, M_n, are available from eq 24 and 27 given below. This distribution has already a more complex character[4,8] compared with the number distribution. Furthermore, the number and weight fractions of macromolecules which do not carry any graft (ungrafted backbones) are respectively

$$N(0) = r^{y_A}$$

$$W(0) = r^{y_A+1} x_w \tag{12}$$

where x_w is the chemical composition of the copolymer (cf. eq 28) given by the weight fraction of the backbone component A.

The distribution functions for a true copolymer, i.e., graft copolymer, from which ungrafted backbones have been separated, are obtained by renormalization ensuing from the number or mass balance

$$N^\dagger(m) = N(m)/(1 - N(0))$$

$$W^\dagger(m) = W(m)/(1 - W(0)) \tag{13}$$

From here onward, quantitites related to the true copolymer are marked with a dagger.

A graphic characteristic following from the distribution function (10) is the number-average number of grafts attached to the backbones (including ungrafted backbones for which $m = 0$), m_n. This average, and the number-average number of grafts in the true copolymer, $m^\dagger_n$, is given by the mean value of the negative binomial distribution

$$m_n = \sum_{m=0}^{\infty} mN(m) = qM^*_{nA}$$

$$m^\dagger_n = \sum_{m=1}^{\infty} mN^\dagger(m) = m_n/(1 - N(0)) \tag{14}$$

If the initial set of backbones has the most probable distribution, i.e., $y_A = 1$, both averages are related by[3]

$$m^\dagger_n = m_n + 1 \tag{15}$$

Molecular Weight Distribution. (a) Backbones. If the parent polymer which is grafted has the Γ-distribution of molecular weights (1), then, according to eq 4, 5, and 7

$$N_A(M_A|m) = \frac{p(m; qM_A)}{n(m; y_A, r)} \Gamma(M_A; y_A, h_A) \tag{16}$$

Hence, the number and weight molecular weight distributions of backbones carrying just m grafts are again given by a Γ-distribution

$$N_A(M_A|m) = \Gamma(M_A; y_A + m, h_A + q)$$

$$W_A(M_A|m) = \Gamma(M_A; y_A + m + 1, h_A + q) \tag{17}$$

Molecular weight averages of backbones in copolymer macromolecules with m grafts ensue from the properties of the Γ-distribution:

$$M_{nA}(m) = \frac{y_A + m}{h_A + q}$$

$$M_{wA}(m) = \frac{y_A + m + 1}{h_A + q} \tag{18}$$

These equations show, among other things, that molecular weights of ungrafted backbones ($m = 0$) decrease with proceeding grafting (increasing q), but the width of their distribution remains unchanged.

(b) Grafts. The distribution functions of molecular weights of the graft parts composed of m grafts (i.e., of the sum of molecular weights of all grafts which form the particular graft parts) are again given by a Γ-type distribution[4,9]

$$N_B(M_B|m) = \Gamma(M_B; my_B, h_B)$$

$$W_B(M_B|m) = \Gamma(M_B; my_B + 1, h_B) \tag{19}$$

Formally identical distribution functions describe also the distribution of star-shape formations which arise by joining m chains having a Γ-distribution of molecular weights.[4] Thus, the molecular weight averages of the graft part of the individual copolymer species are given by

$$M_{nB}(m) = my_B/h_B = mM^*_{nB}$$

$$M_{wB}(m) = (my_B + 1)/h_B \tag{20}$$

The total molecular weight distribution of graft parts in the copolymer is given by the weighted sum of distributions of the individual copolymer species; it cannot, however, be expressed in a closed form but only as a series.[9] On the other hand, explicit relations can be derived for molecular weight averages of the whole graft parts of the true copolymer:

$$M^\dagger_{nB} = m^\dagger_n M^*_{nB}$$

$$M^\dagger_{wB} = qM^*_{nB}M^*_{wA} + M^*_{wB} \tag{21}$$

(c) Copolymer. If the molecular weight distributions of backbones and of the graft parts of copolymer species are given by a Γ-distribution according to eq 17 and 19, then the distribution of molecular weight, M, of copolymer macromolecules again cannot be expressed in a closed form. Molecular weight averages of a given copolymer species can be derived irrespective of the concrete form of the distribution function. We have

$$M_n(m) = \int_{M_A}\int_{M_B} (M_A + M_B)N_A(M_A|m)N_B(M_B|m)\, dM_A\, dM_B \tag{22}$$

and

$$M_w(m)M_n(m) = \int_{M_A}\int_{M_B}(M_A + M_B)^2 N_A(M_A|m)N_B(M_B|m)\,dM_A\,dM_B \quad (23)$$

Integration yields

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

$$M_w(m) = x_w(m)M_{wA}(m) + [1 - x_w(m)]M_{wB}(m) + 2x_w(m)[1 - x_w(m)]M_n(m) \quad (24)$$

where, recalling eq 18 and 20

$$x_w(m) = M_{nA}(m)/M_n(m) = \left(1 + \frac{my_B(h_A + q)}{(y_A + m)h_B}\right)^{-1} \quad (25)$$

is the average chemical composition of the given copolymer species.

Similarly, for molecular weights of the whole copolymer we have

$$M_n = \sum_m M_n(m)N(m)$$

$$M_wM_n = \sum_m M_w(m)M_n(m)N(m) \quad (26)$$

Summation gives[4,8]

$$M_n = M^*_{nA} + m_nM^*_{nB}$$

$$M_w = M^*_{wA}/x_w + M^*_{wB}(1 - x_w) \quad (27)$$

where $x_w = M_{nA}/M_n$ is the average composition of the copolymer given by the fraction of the backbone part which is related to the grafting parameter q by

$$x_w = (1 + qM^*_{nB})^{-1} \quad (28)$$

Distribution of Chemical Composition. The chemical composition of the individual copolymer macromolecules given by the weight fraction of component A is $x = M_A/(M_A + M_B)$. For copolymer species satisfying the model discussed here, the differential weight distribution function of chemical composition may be derived[9] in the form

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

By introducing the substitution

$$z = \frac{h_Ax}{h_Ax + h_B(1 - x)}$$

the distribution function of chemical composition may be rewritten in a more graphic form as a linear combination of two B-distributions

$$W(x|m)\,dx = [x_w(m)B(z; y_A + m + 1, my_B) + (1 - x_w(m))B(z; y_A + m, my_B + 1)]\,dz \quad (30)$$

$x_w(m)$ is the average chemical composition of the copolymer species given by eq 25, and the B-distribution of the variable z is generally defined as

$$B(z; y_A, y_B) = \frac{\Gamma(y_A + y_B)}{\Gamma(y_A)\Gamma(y_B)}z^{y_A-1}(1 - z)^{y_B-1}$$

where y_A and y_B are parameters.

The distribution function (29) or (30) is an important result of this study. After substitution of the respective parameters,[9] the function can also be used in the description of block copolymer species. The distribution function of chemical composition for the true copolymer can be calculated by weighted summation of the distribution functions of chemical composition of the individual copolymer species (see eq 29)

$$W^\dagger(x) = \sum_{m=1}^{\infty} W(x|m)W^\dagger(m) \quad (31)$$

Chemical heterogeneity of the true copolymer can be characterized, e.g., by the variance of chemical composition

$$(\sigma^2)^\dagger = \int_x (x - x_w^\dagger)^2 W^\dagger(x)\,dx \quad (32)$$

which describes the width of distribution of chemical composition of copolymer chains.

Table I
Model Dependence of Selected Characteristics of the Graft Copolymer on the Extent of Grafting Quantified by the Weight Fraction of Grafted Backbones, $1 - W_A(0)$[a]

	$1 - W_A(0)$			
	0.2	0.4	0.6	0.8
True Copolymer				
$M^\dagger_{nA} \times 10^{-3}$	189	177	163	144
$M^\dagger_{nB} \times 10^{-3}$	111	129	158	223
$M^\dagger_n \times 10^{-3}$	300	306	321	367
$M^\dagger_{wA} \times 10^{-3}$	284	267	249	227
$M^\dagger_{wB} \times 10^{-3}$	223	258	316	447
$M^\dagger_w \times 10^{-3}$	410	432	478	603
$\gamma^\dagger_A$	1.50	1.50	1.52	1.57
$\gamma^\dagger_B$	2.00	2.00	2.00	2.00
$\gamma^\dagger$	1.36	1.40	1.49	1.63
$x^\dagger_w$	0.629	0.579	0.508	0.393
$m^\dagger_n$	1.118	1.290	1.581	2.236
$(\sigma^2)^\dagger \times 10^2$	6.31	5.83	5.15	3.78
Graft Copolymer (Including Ungrafted Backbones)				
$M_n \times 10^{-3}$	111	129	158	223
$M_w \times 10^{-3}$	244	303	389	557
γ	2.18	2.34	2.46	2.49
x_w	0.894	0.775	0.632	0.447
m_n	0.118	0.290	0.581	1.236

[a] Molecular weights of the initial set of backbones and attendant graft homopolymer were taken as $M^*_{wA} = M^*_{wB} = 2 \times 10^5$ and $M^*_{nA} = M^*_{nB} = 1 \times 10^5$. $M^\dagger_{nA}$, $M^\dagger_{nB}$, and $M^\dagger_n$, and $M^\dagger_{wA}$, $M^\dagger_{wB}$, $M^\dagger_w$ are respectively number- and weight-average molecular weights of the backbone and graft parts of the true copolymer and of the true copolymer as a whole, $\gamma^\dagger_A$, $\gamma^\dagger_B$, and $\gamma^\dagger$ are the respective ratios of the weight- and number-average molecular weights, x_w is chemical composition given by the weight fraction of the backbone part, $m^\dagger_n$ is the number-average number of grafts, and $(\sigma^2)^\dagger$ is the variance of composition of the true copolymer. Quantities without a dagger characterize analogously the whole graft copolymer.

Model Calculations

Using, as an example, a model system in which both the parent backbone homopolymer and the attendant graft homopolymer have the same molecular weight distribution (given by the most probable distribution for the sake of simplicity), changes can be demonstrated in the individual characteristics with proceeding grafting (Table I). The degree of grafting is quantified by the weight fraction of grafted backbones, $1 - W_A(0)$.

It can be seen, for instance, that changes in the molecular weight of the true copolymer, $M^\dagger_n$ and $M^\dagger_w$, are comparatively small, and values of these quantities increase only at high fractions of grafted backbones. The cause lies in the fact that, although the molecular weight of the graft

Table II
Preparation Conditions of Graft Copolymers Polystyrene-*g*-poly(methyl methacrylate) and Composition of the Rough Product[a]

sample	irradiation time, min	temp, °C	conversion of MMA, wt %	content of components in the rough product, wt %		
				PS	PMMA	copolymer
A	130	30	5.2	11	53	36
B	240	30	14.0	2	73	25
C	130	40	10.6	4	65	31
D	150	30	8.8	2	59	39
E	210	30	10.1	2	64	34
F	110	30	3.1	19	44	37

[a] Parent polystyrene: samples A-C, $M^*_{nA} = 83 \times 10^3$, $M^*_{wA} = 200 \times 10^3$; samples D-F, $M^*_{nA} = 365 \times 10^3$, $M^*_{wA} = 730 \times 10^3$.

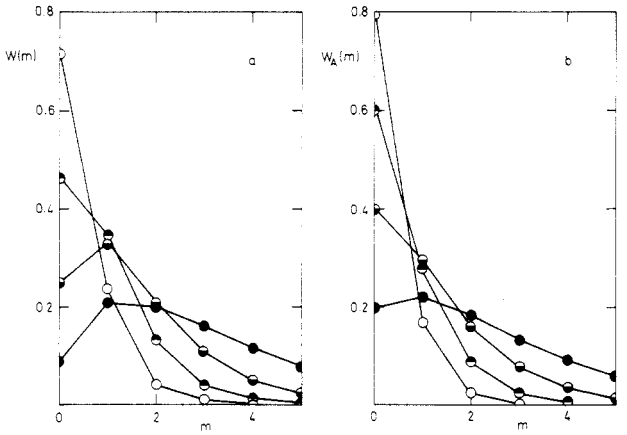

Figure 2. Weight fraction of (a) copolymer macromolecules with m grafts, $W(m)$, and (b) backbones carrying m grafts, $W_A(m)$, for various degrees of grafting given by the weight fraction of grafted backbones, $1 - W_A(0)$. $1 - W_A(0) = 0.2$ (○), 0.4 (◓), 0.6 (◒), and 0.8 (●); $M^*_{wA} = M^*_{wB} = 2 \times 10^5$, $M^*_{nA} = M^*_{nB} = 1 \times 10^5$.

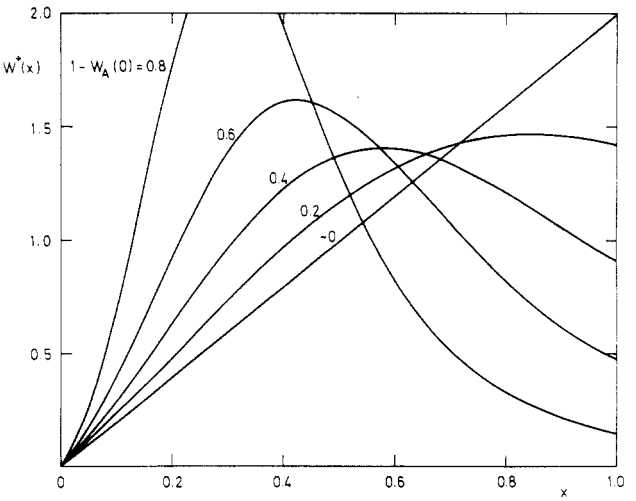

Figure 3. Differential weight distribution function of chemical composition, $W^\dagger(x)$, of true graft copolymer for various degrees of grafting given by the weight fraction of grafted backbones marked at the individual curves. $M^*_{wA} = M^*_{wB} = 2 \times 10^5$, $M^*_{nA} = M^*_{nB} = 1 \times 10^5$.

part, e.g., $M^\dagger_{nB}$, increases quickly, that of the backbone part, e.g., $M^\dagger_{nA}$, gradually decreases (backbones of the highest molecular weight have become predominantly part of the copolymer, while those of lower molecular weight are grafted to a major extent only in the later stage).

The polydispersity index of the backbone part of the true copolymer, $\gamma^\dagger_A = M^\dagger_{wA}/M^\dagger_{nA}$, gradually increases (Table I), until eventually, when all backbones are grafted by at least one graft chain, it might reach the limiting value of the polydispersity index of the parent polymer (here, $\gamma^*_A = 2$). In our case, where both parent and graft polymer are assumed to have the most probable molecular weight distribution, the same polydispersity of the graft part, viz., $\gamma^\dagger_B = 2$, is found independently of the degree of grafting.

The chemical heterogeneity of the true copolymer characterized by the variance of chemical composition, $(\sigma^2)^\dagger$, decreases, as expected, with increasing degree of grafting. It is larger than the chemical heterogeneity usually observed with statistical copolymers. The average numbers of attached grafts in the copolymer, m_n, and in the true copolymer, $m^\dagger_n$, are related in a simple manner given by eq 15.

Figure 2 shows the weight distribution of the individual copolymer species and its changes with increasing degree of grafting. The fraction of macromolecules containing a major number of grafts can be seen to become significant only at a relatively high degree of grafting. This conclusion is qualitatively supported also by the shape of the distribution functions of chemical composition (Figure 3) calculated with eq 31. The distribution function represented in Figure 3 by a straight line corresponds to the limiting case of an infinitesimally small degree of grafting.

The course of the functions also suggests that, at a low degree of grafting, the true copolymer contains a considerable fraction of macromolecules which by their composition are close to the parent backbone polymer; i.e., $x \rightarrow 1$. In these cases, separation of ungrafted backbones would present a considerable experimental problem. In principle, the attendant graft polymer should be easier to separate, although its relative amount present in the rough product may also play an important role. Theoretically, the possibility of an efficient separation of the two homopolymers becomes better with increasing degree of grafting, because the distribution of chemical composition becomes gradually narrower (Figure 3). In practice, however, this effect, favorable on the whole, may be compensated by the liability of grafted macromolecules to form micellar structures in the process of separation of the homopolymers; these structures may solubilize the homopolymers,[10] and the extent of solubilization is likely to increase with the increasing fraction of the grafted copolymer. Hence, prospects of perfect separation of the homopolymer from the true copolymer are not too bright.

We made an attempt to confront the theoretical predictions exposed in this study with the experimental characterization of graft copolymers of polystyrene backbone and poly(methyl methacrylate) grafts.

Experimental Section

Graft copolymers polystyrene-*g*-poly(methyl methacrylate) were prepared by a method according to Jones.[11] Bromine radicals are split by UV irradiation from polystyrene (PS) macromolecules, partly brominated on the α-carbon. Radicals formed on PS chains

Table III
Experimental Characterization of Copolymers Polystyrene-g-poly(methyl methacrylate)

	sample						
	A	B	C	D	E	F	method[b]
Molecular Weights of Homopolymers and Composition of the Copolymer (Input Data for Calculation)							
$M^*_{nA} \times 10^{-3}$	83	83	83	365	365	365	OP
$M^*_{wA} \times 10^{-3}$	200	200	200	730	730	730	LS
$M^*_{nB} \times 10^{-3}$	115	177	170	138	150	114	OP
$M^*_{wB} \times 10^{-3}$	250	480	470	330	330	250	LS
x_w	0.615	0.356	0.425	0.473	0.490	0.717	EA
"True" Copolymer							
$M^\dagger_n \times 10^{-3}$	226	299	350	1010	800	650	OP
$M^\dagger_w \times 10^{-3}$	450	960	980	1910	1600	810	LS
$M^\dagger_{nA} \times 10^{-3}$	109	91	122	456	353	417	calcd[a]
$M^\dagger_{wA} \times 10^{-3}$	220	280	340	1010	880	690	LS
$M^\dagger_{nB} \times 10^{-3}$	117	208	228	553	447	233	calcd[a]
$M^\dagger_{wB} \times 10^{-3}$	250	690	640	1030	740	700	LS
$x^\dagger_w$	0.483	0.305	0.348	0.452	0.441	0.641	EA
$m^\dagger_n$	1.01	1.17	1.34	3.87	2.98	2.04	calcd[a]
Ungrafted Backbones							
$M_{wA}(0) \times 10^{-3}$	90	60	70	160	190	270	LS
$W_A(0)$	0.431	0.528	0.389	0.140	0.167	0.347	EX

[a] $M^\dagger_{nA} = x^\dagger_w M^\dagger_n$; $M^\dagger_{nB} = (1 - x^\dagger_w)M^\dagger_n$; $m^\dagger_n = M^\dagger_{nB}/M^*_{nB}$. [b] Methods: OP, osmotic pressure; LS, light scattering; EA, elemental analysis; EX, extraction.

initiate the growth of grafts in the presence of monomeric methyl methacrylate. In all cases we started with a mixture consisting of 1.7 wt % brominated PS (with each 51st–55th monomeric unit being brominated), 72.5 wt % methyl methacrylate, and 25.8 wt % benzene. A high-pressure mercury discharge tube (250 W) was placed at a distance of 0.5 m. The attendant graft homopolymer, poly(methyl methacrylate) (PMMA), was removed from the rough copolymer product by twofold extraction with acetonitrile. PS was similarly removed by extraction with cyclohexane.[12] The residue after the extraction was regarded as the true copolymer.

Compositions of the graft copolymer (containing the backbone homopolymer) and of the true copolymer were determined by elemental analysis. Number-average molecular weights of the starting parent polymer, of the graft homopolymer, and of the copolymer were determined in toluene at 35 °C with a dynamic membrane osmometer, Hewlett-Packard, Type 502. Weight-average molecular weights were determined by light scattering with a Sofica 42.000 apparatus as described elsewhere.[13] In the direct molecular weight determination of the individual parts of the true copolymer, solvents isorefractive with the other part of the copolymer were used, viz., mixtures of α-bromonaphthalene and butanone, 80:20 by volume, for the graft (PMMA) part and 42.5:57.5 by volume for the backbone part (PS). Refractive index increment values at a fixed chemical potential of the solvent components were taken from the literature.[13]

Results and Discussion

Results of the experimental characterization of the true copolymer are given in Table III; in Table IV, these data are compared with values calculated by relations given in the Theoretical Section. The input characteristics for the calculation were molecular weights of the parent and graft homopolymers and composition of the graft copolymer (Table III), which reflects the degree of grafting.

The PMMA content in the rough copolymer product is surprisingly high (Table II). Unless all the graft homopolymer is removed, the copolymer composition found by analysis (given by the weight fraction of the backbone part) is lower than the true one. Due to skewed input data, calculation using the above model concepts leads to a degree of grafting higher than the correct value (cf. $m^\dagger_n$ in Table IV). Similarly, calculation carried out under these circumstances would predict that all molecular weights which increase with the increasing degree of grafting ($M^\dagger_n$, $M^\dagger_w$, $M^\dagger_{nB}$, and $M^\dagger_{nB}$) will be higher, while all those which decrease with proceeding grafting ($M^\dagger_{nA}$ and $M^\dagger_{wA}$) would

Table IV
Comparison between Experimental Results and Characteristics Obtained by Model Calculations[a]

	sample					
	A	B	C	D	E	F
$M^\dagger_n$	1.48	1.65	1.29	0.99	1.08	1.21
$M^\dagger_w$	1.18	0.99	0.86	0.92	1.07	1.49
$M^\dagger_{nA}$	1.47	1.57	1.23	1.00	1.33	1.26
$M^\dagger_{wA}$	1.17	0.85	0.72	0.76	0.88	1.20
$M^\dagger_{nB}$	1.50	1.69	1.32	0.98	1.18	1.11
$M^\dagger_{wB}$	1.50	1.23	1.16	1.11	1.47	0.77
$x^\dagger_w$	0.99	0.95	0.95	1.01	1.06	1.05
$m^\dagger_n$	1.51	1.71	1.34	1.02	1.18	1.11
$M_{wA}(0)$	1.35	1.50	1.50	1.16	1.08	1.19
$W_A(0)$	0.98	0.49	0.83	0.46	0.48	0.56

[a] Tabulated values represent ratio of the calculated quantity to the experimental one.

be lower. Thus, the presence of a remainder of unseparated PMMA in the true copolymer may account for most of the differences between the calculated and experimental values.

The experimentally determined weight fraction of ungrafted polystyrene backbones removed by extraction is higher than predicted (Table IV). As has been discussed in connection with model calculations (Figure 3), it is likely that copolymer macromolecules with a high content of the backbone part are removed along with the ungrafted backbones, which would result in a further apparent rise in the degree of grafting. To be sure, the absolute weight amounts of ungrafted backbones are very small and, due to the low content of the parent polymer in the reaction mixture, their isolation and determination are subjected to a considerable error.

Bearing in mind the difficult separation of the individual components of the rough copolymer product and exacting methodical requirements involved in the determination of the individual characteristics of the true graft copolymer (e.g., the weight-average molecular weight must be determined by light scattering measurement in three different solvents), the fit between experimental data and theoretical prediction may be regarded as acceptable. On the other hand, as has been suggested by model calculations, a number of characteristics of the copolymer depend

rather little on the degree of grafting, especially if the latter is low. For this reason, it cannot be decided unambiguously if the grafting model discussed here is completely adequate to physical reality. No papers concerned with a detailed experimental study of molecular parameters of graft copolymers could be found in the literature. It is believed, therefore, that any contribution dealing with the subject may appear useful.

Registry No. (Methyl methacrylate)·(styrene) (copolymer), 25034-86-0.

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Characterization of Poly(methyl methacrylate) during the Thermal Polymerization of Methyl Methacrylate

Ben Chu* and Day-chyuan Lee

Chemistry Department, State University of New York at Stony Brook, Long Island, New York 11794.

Received August 11, 1983

ABSTRACT: During the thermal polymerization of MMA, we have been able to investigate both the static and the dynamic properties of the polymer formed, poly(methyl methacrylate) (PMMA), in terms of the molecular weight M_w, the second virial coefficient A_2, the radius of gyration R_g, the translational diffusion coefficient D_T and its corresponding equivalent hydrodynamic radius R_h, and estimates of the size (or molecular weight) distribution of PMMA in dilute solution and in terms of the isothermal compressibility $(\partial\pi/\partial C)_{P,T}$, the cooperative diffusion coefficient D_c, and a slow characteristic decay time which mimics but is not the self-diffusion coefficient D_s in the semidilute solution regime. By combining a spectroscopic technique such as Raman scattering, which can determine the polymer concentration noninvasively during the polymerization process, with laser light scattering, we have demonstrated a viable procedure for on-line monitoring of solution polymerization processes, permitting us to investigate detailed macromolecular properties in solution polymerization kinetics.

I. Introduction

Studies of polymerization processes have been difficult because we lack a convenient probe which we can use one-line to monitor the concentrations of the monomer(s) and of the polymer in a polymerization reaction. Spectroscopic techniques such as NMR, IR, Raman, and fluorescence and other physical methods such as density and surface tension offer reasonable and possible alternatives which permit us to measure the appropriate concentration of species in a chemical reaction. However, in a polymerization process, we really want to know not only the concentrations of the monomer (C_m) and of the polymer (C_p) but also molecular parameters such as the molecular weight M of the polymer product during the chemical reaction.

The aim of this article is directed at an important need in chemical reactor engineering; i.e., we try to link together an application of several established results in Raman scattering and laser light scattering and hopefully to demonstrate that development of an on-line technique for characterizing the polymer product during the course of the polymerization reaction is a worthwile undertaking even though it is likely to be a difficult one from practical viewpoints. Nevertheless, as informative on-line measurements of important molecular parameters of the polymer product often represent the major stumbling block to control of polymerization processes, an establishment of measurements on accessible molecular parameters of the polymer product in our proposed scheme under even ideal conditions becomes of interest.

It should be recognized that our measurement scheme is limited mainly to solution and bulk polymerization processes and that we have neglected convective motions which often exist in a chemical reactor. Such convective motions, which could be produced by flow of reactant(s) and product(s) and/or by thermal gradients, would invariably affect the light scattering spectrum and the translational diffusive motions of the polymer product(s). However, these problems may be resolved by varying experimental conditions or they can be investigated for specific systems. For example, flow can be measured by using laser Doppler velocimetry[1] and thermal gradients can be alleviated by changing the chemical reaction vessel design.

In this paper, we report some of the results of our studies on the thermal polymerization of methyl methacrylate (MMA) using a combination of Raman scattering and laser light scattering[1] whereby we have been able to measure many of the main variables of interest in terms of known molecular parameters, namely, the rate of conversion, the weight-average molecular weight M_w of the polymer product, poly(methyl methacrylate) (PMMA), and esti-

0024-9297/84/2217-0926$01.50/0