

Compositional Heterogeneity and Molecular Weight Distribution of Copolymer Systems

I. Simple Statistical Analysis of the Heterogeneities of Block and Graft Copolymers

Tadao KOTAKA, Nobuo DONKAI,* and Tae Ik MIN.**

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Expressions of various average molecular weights including light-scattering apparent values, compositional heterogeneity and molecular weight distribution have been derived for block and graft copolymers by applying, respectively, the random-coupling, and the random-grafting statistics. The average molecular weights may be correlated with certain easily accessible experimental data. The relations provide important criteria for checking the heterogeneity of the material under investigation.

In particular it was shown that the complete description of compositional heterogeneity and molecular weight distribution may be obtained from the following experimental data:

- i) The overall chemical composition.
- ii) Molecular weight distributions of constituent homopolymers, *i. e.*, for a block copolymer those of the two precursor homopolymers, and for a graft copolymer those of the backbone prepolymer and of the graft-side-chains which may or may not be identical to that of the ungrafted side-chain homopolymer separable from the reaction mixture.
- iii) For a graft copolymer the true graft ratio or the grafting efficiency.
- iv) And for a mixed block copolymer the type and the relative amount of each species involved, which may be deduced from the reaction mechanism and kinetics.

INTRODUCTION

Compositional heterogeneity and molecular weight distribution are important factors for characterizing physical properties of copolymers. Nevertheless, careful studies on the heterogeneities of copolymers appear to be rather sparse. Immediately after the now well-known theory of addition copolymerization¹⁻⁴⁾ was first presented, several authors developed the theory to describe the compositional heterogeneity and molecular weight distribution of addition copolymers.⁵⁻⁷⁾ However, it is of rather recent event that these earlier theories have been seriously tested and proved to be generally valid.⁸⁻¹¹⁾ This situation appears to have been resulted from the difficulty and tediousness in carrying out the experimental analysis. This is to be contrasted to the microstructural analysis of copolymers and stereospecific polymers mostly based on a highly sophisticated technique of high resolution nuclear-magnetic-resonance spectroscopy.^{12,13)} Upon carrying out nmr measurements and subsequent microstructural analysis one often ignores the heterogeneity of the material one is dealing with. However, occasionally careful characterization

* 小高忠男, 吞海信雄: Laboratory of Polymer Characterization, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

** 閔 泰益: On leave from Department of Polymer Engineering, College of Engineering, Pusan National University, Pusan, Korea.

study reveals that a material which has been believed (without reason) to be a single component could be in fact a mixture or a complex of entirely different species.¹⁴⁾ Thus the ignorance of characterizing the heterogeneity could lead to an erroneous conclusion. Anyway the ease and the sophistication of nmr have stimulated the development of the copolymerization theory to describe microstructural characteristics of copolymers¹³⁾ which of course has been embraced in the original theory.¹⁻⁴⁾

Another drawback in carrying out the copolymer heterogeneity analysis arises from the fact that many experimental techniques such as light-scattering,¹⁵⁻¹⁷⁾ gel permeation chromatography (gpc),^{18,19)} *etc.* have poor sensitivity and can provide only limited information on the copolymer heterogeneity. For example, use of a dual detector in gpc provides an information only on point-by-point composition at each constant elution volume level.¹⁹⁾ In order to deduce a detailed information from these experiments, one has to have an adequate theory which correlates the measurable quantities with the copolymer heterogeneity. Still another difficulty is expected in the interpretation of experimental data. For example, equilibrium sedimentation in a density gradient²⁰⁾ provides an excellent technique of detecting heterogeneity of copolymer sample. However, the quantitative interpretation of the result is not at all easy because of many complicating factors.²⁰⁾ Here again it seems to be easier to deduce an equilibrium band shape from the knowledge of the sample heterogeneity rather than to do the reverse.

The advent of graft and block copolymers in practical application such as high impact plastics and thermoplastic elastomer^{21,22)} have led to a new problem in the copolymer heterogeneity analysis. Apparently the heterogeneity of graft and block copolymers cannot be described by the theory of addition copolymerization. Experimental techniques which have been successful for random copolymers might not be effective for graft and block copolymers: Fractionation encounters a difficulty of coprecipitation or coelution of more than one components.^{21,23)} Thin-layer chromatographic (tlc) separation¹¹⁾ also is hampered by this phenomenon and by conformational anomalies which alter the adsorption characteristics of graft and block copolymers onto substrate (usually silica gel) surfaces.^{24,25)} High resolution nmr is useless for analyzing extent of grafting or blocking, unless they exist in very high frequencies.

In this series of studies we have attempted to examine copolymerization theories (including existing ones) and methods of the heterogeneity analysis. The purpose is twofold: (i) One is to find out the features of the compositional heterogeneity and molecular weight distribution of a copolymer in relation to the copolymerization mechanism and kinetics; and (ii) the other is to establish methods of deducing the features of the copolymer heterogeneity from a minimal amount of accessible information. In this first paper we examine the compositional heterogeneity (CH) and molecular weight distribution (MWD) functions of linear block copolymers (of arbitrary block number) and of graft copolymers, assuming that the MWDs of individual subchains are mutually independent. For block copolymer we assume that the polymerization proceeds through random coupling mechanism, *i.e.*, the reactivity of active terminals of precursor homopolymers is independent of their molecular weight. This model corresponds to those obtained by anionic living polymerization method^{21,26,27)} and also by coupling reaction between complementary active terminals of precursor homopolymers.^{21,28)} For graft copolymer we assume that grafting is completely random, *i.e.*, all segments of the backbone chains have equal prob-

ability to be grafted, and also that any side reactions such as backbone breakdown and cross-linking do not take place. Admittedly these assumptions are too crude to be valid for many practical examples. However, the analysis would have some value for certain simple cases.^{21,29)}

AVERAGE MOLECULAR WEIGHTS

Number-average molecular weight: We consider an AB-binary copolymer system. Determination of number-average molecular weight M_n based on colligative properties measurements can be applied, in principle, without any ambiguity to any heterogeneous system. Likewise average composition $\bar{x}$ (by weight fraction of component A) of the copolymer can be determined without ambiguity. In terms of the CH and MWD function, we have

$$M_n = \int_0^\infty \int_0^1 MN(x, M) dx dM \quad (1)$$

$$\bar{x} = \int_0^\infty \int_0^1 xW(x, M) dx dM \quad (2)$$

where $N(x, M)dx dM$ and $W(x, M)dx dM$, respectively, represent the number- and weight-fraction of component having molecular weight M and composition x . These two distributions are related by

$$W(x, M)dx dM = (M/M_n)N(x, M)dx dM \quad (3)$$

Here we introduce experimentally measurable quantities M_n^A and M_n^B as

$$M_n^A = \int_0^\infty \int_0^1 xMN(x, M)dx dM = \bar{x}M_n \quad (4a)$$

$$M_n^B = (1 - \bar{x})M_n \quad (4b)$$

These quantities alone cannot tell anything about the sample heterogeneity except for certain special cases as will be discussed later.^{30,31)}

Weight-average molecular weight: For an AB-binary copolymer weight-average molecular weight M_w can be defined as

$$M_w = \int_0^\infty \int_0^1 MW(x, M)dx dM \quad (5a)$$

which is written as

$$M_w = \bar{x}M_w^A + (1 - \bar{x})M_w^B + 2M_w^{AB} \quad (5b)$$

$$\bar{x}M_w^A = \int_0^\infty \int_0^1 x^2MW(x, M)dx dM \quad (5c)$$

$$(1 - \bar{x})M_w^B = \int_0^\infty \int_0^1 (1 - x)^2MW(x, M)dx dM \quad (5d)$$

$$M_w^{AB} = \int_0^\infty \int_0^1 x(1 - x)W(x, M)dx dM \quad (5e)$$

The quantities M_n^K and M_w^K ($K=A$ or B) are the number and weight-average molecular weights, respectively, of the K -component. However, these do not represent the individual subchains but the sum of all K -segments in each copolymer chain. The correlation between these two sets of average molecular weights will be discussed later. The significance of the quantity M_w^{AB} is not clear, until a specific model is defined to describe the system. For example, it is zero for a mixture of two homopolymers.

Light-scattering apparent molecular weight: For a copolymer especially having compositional heterogeneity the light-scattering method has fundamental difficulty.^{15,16)} This is also true for conventional sedimentation equilibrium method.³²⁾ Nevertheless, these methods are only reliable ones for determining M_w of heterogeneous copolymers.

We assume linear dependence of specific refractive-index increment ν of a copolymer on composition $\bar{x}$

$$\nu = \bar{x}\nu_A + (1-\bar{x})\nu_B \quad (6)$$

Then one can write light-scattering apparent molecular weight¹⁶⁾ M_{app} as determined by the procedure of Zimm³³⁾ as follows

$$M_{app} = \nu^{-2} [\bar{x}M_w^A\nu_A^2 + (1-\bar{x})M_w^B\nu_B^2 + 2\nu_A\nu_B M_w^{AB}] \quad (7)$$

where ν_K represents the value of homopolymer K . The quantity M_{app} can also be written in the form^{15,16)}

$$M_{app} = M_w + 2bP + b^2Q \quad (8a)$$

$$\begin{aligned} P &= \int_0^\infty \int_0^1 (x-\bar{x})MW(x, M)dx dM \\ &= \bar{x}(1-\bar{x})(M_w^A - M_w^B) + (1-2\bar{x})M_w^{AB} \end{aligned} \quad (8b)$$

$$\begin{aligned} Q &= \int_0^\infty \int_0^1 (x-\bar{x})^2 MW(x, M)dx dM \\ &= \bar{x}(1-\bar{x})[(1-\bar{x})M_w^A + \bar{x}M_w^B - 2M_w^{AB}] \end{aligned} \quad (8c)$$

$$b = (\nu_A - \nu_B)/\nu \quad (8d)$$

All these equations (1)–(8) have been derived without introducing any assumptions except that of Eq. (6), which has been experimentally justified.^{15,16)} Therefore, these equations should be generally valid for any copolymer systems. As opposed to M_n^K , the quantity M_w^K cannot be easily determined. However, Eq. (7) shows that light-scattering measurements in a solvent isorefractive to one component (*i.e.*, $\nu_j=0$) allows one to determine M_w^K of the other component K . Usually measurements at least in three different solvents are necessary to determine the parameter P and Q including M_w itself. These parameters are often insensitive, but can represent to some extent the heterogeneity of the copolymer sample.¹⁷⁾

HETEROGENEITY OF LINEAR BLOCK COPOLYMERS

Random Coupling Statistics

The CH- and MWD-function: We consider a multiblock copolymer consisting of m and n pieces of A and B blocks, respectively. (Usually $m=n$ or $|m-n|=1$.) Let

$N_K(M)dM$ represent the normalized number-based MWD of individual K blocks. We assume that all $N_K(M)$'s of the type K are identical and coupling of the precursor chains proceeds completely in random fashion. In other words, all active ends have equal opportunity of coupling irrespective of their chain lengths. With these assumptions the normalized number-based frequency of a species having $M=M_A+M_B=(M_1+M_2+\dots+M_m)_A+(M_1+M_2+\dots+M_n)_B$ will be

$$\begin{aligned} N(M_1, M_2, \dots, M_{m+n})dM_1dM_2\dots dM_{m+n} \\ = \prod_{i=1}^m N_A(M_i)dM_i \prod_{j=1}^n N_B(M_j)dM_j \end{aligned} \quad (9)$$

and the weight-based frequency is $W(\dots)dM_1dM_2\dots dM_{m+n}=(M/M_n)N(\dots)dM_1dM_2\dots dM_{m+n}$. Using the relations $M_A=xM$ and $M_B=(1-x)M$, we have, for example, the weight-based CH- and MWD-function

$$\begin{aligned} W(x, M)dx dM \\ = (M^2/M_n) \left\{ \int_0^{xM} N_A(M_1)dM_1 \int_0^{xM-M_1} N_A(M_2)dM_2 \dots \right. \\ \left. \int_0^{xM-M_1-\dots-M_{m-2}} N_A(M_{m-1})N_A(xM-M_1-\dots-M_{m-1})dM_{m-1} \right. \\ \left. \int_0^{(1-x)M} N_B(M_1)dM_1 \int_0^{(1-x)M-M_1} N_B(M_2)dM_2 \dots \right. \\ \left. \int_0^{(1-x)M-M_1-\dots-M_{n-2}} N_B(M_{n-1})N_B[(1-x)M-M_2-\dots-M_{n-1}]dM_{n-1} \right\} dx dM \quad (10) \end{aligned}$$

If the MWDs of the precursors are known, the integration of Eq. (10) can be carried out numerically by the aid of a computer. If the MWDs can be expressed by analytical functions such as the Schulz MWD-function,³⁴⁾ the most probable distribution,³⁵⁾ the Poisson distribution,³⁵⁾ etc., the calculation is much simpler.

Average molecular weights: Certain average quantities can be calculated from Eq. (10) without any explicit knowledge of the $N_K(M)$ functions. For example, we have following equations for $\bar{x}$, $\bar{M}_n$, and $\bar{M}_w$ of a (m, n)-multiblock copolymer

$$\bar{x} = m\bar{M}_n^A / M_n \quad (11a)$$

$$M_n = m\bar{M}_n^A + n\bar{M}_n^B \quad (11b)$$

$$\begin{aligned} M_w = \bar{x}[\bar{M}_w^A + (m-1)\bar{M}_n^A] \\ + (1-\bar{x})[\bar{M}_w^B + (n-1)\bar{M}_n^B] + 2\bar{x}(1-\bar{x})M_n \end{aligned} \quad (11c)$$

where $\bar{M}_n^K$ and $\bar{M}_w^K$ are those of the precursor K (K=A or B)

$$\bar{M}_n^K = \int_0^\infty MN_K(M)dM \quad (12a)$$

$$\bar{M}_w^K = \int_0^\infty MW_K(M)dM \quad (12b)$$

Comparing Eqs (4), (5), (11), and (12), we see that

$$M_n^K = (\text{number of K-blocks})\bar{M}_n^K \quad (13a)$$

$$M_w^K = \bar{M}_w^K + (\text{number of K-blocks} - 1) \bar{M}_n^K \quad (13b)$$

$$M_w^{AB} = m \bar{M}_n^A n \bar{M}_n^B / M_n = \bar{x}(1 - \bar{x}) M_n \quad (13c)$$

$$Y_K = \bar{Y}_K / (\text{number of K-blocks}) \quad (13d)$$

where Y 's are the MWD indices, *i.e.*, $M_w/M_n = 1 + Y$, *etc.* These equations are combined with Eq (8) to give

$$M_w = (1 + Y) M_n = [1 + \bar{x}^2 Y_A + (1 - \bar{x})^2 Y_B] M_n \quad (14a)$$

$$P = \bar{x}(1 - \bar{x}) [\bar{x} Y_A - (1 - \bar{x}) Y_B] M_n \quad (14b)$$

$$Q = \bar{x}^2 (1 - \bar{x})^2 (Y_A + Y_B) M_n \quad (14c)$$

Then from Eqs. (8) and (14) or from Eqs. (7) and (13), we have

$$M_{app} = \{1 + (\bar{x} \nu_A / \nu)^2 Y_A + [(1 - \bar{x}) \nu_B / \nu]^2 Y_B\} M_n \quad (15a)$$

$$\nu_A / \nu = 1 + b(1 - \bar{x}) \text{ and } \nu_B / \nu = 1 - b\bar{x} \quad (15b, c)$$

Thus if measurements are made in a solvent isorefractive to one component, say, $\nu_B = 0$ or $b = 1/\bar{x}$, we have $M_{app}/M_n = M_w^A/M_n^A$, or if $\nu_A = 0$ or $b = -1/(1 - \bar{x})$, we have $M_{app}/M_n = M_w^B/M_n^B$. Anyway the quantities M_w , P , and Q can be predicted from more easily accessible quantities M_n , $\bar{x}$, and $\bar{Y}_K$'s as far as the random coupling statistics is valid for the system.

The Equations (13) and (14) suggest an interesting feature of the block copolymerization through the random coupling mechanism. As pointed out by Freyss *et al.*,³⁰ the MWD of an AB-diblock copolymer is always smaller than that of its most polydisperse precursor, and often can be even smaller than either of the two precursors. When the number of blocks becomes large, the MWD may become very narrow in comparison with that of the individual blocks. This is due to partial compensating effect of the random coupling mechanism. However, this does not imply that multiblock copolymers may become automatically homogeneous in composition. Coupling of a shorter A-chain with a longer B-chain and *vice versa* narrows the MWD but apparently not the CH-function. In addition to this, in practical cases of multiblock copolymerization the product often turns out to be a mixture of copolymers of different block number, which of course is a highly heterogeneous material.

Mixed Block Copolymers

Average molecular weights and the CH- and MWD function: Practical block copolymerization often leads to the formation of a mixed block copolymer. In such a case the mole fraction n_j of a component j can be related with the copolymerization kinetics. First let us assume n_j be known. We assume that the j -mer consists of j_A -blocks of type A and j_B of type B. Homopolymer contamination is simply defined as a component in which j_A (or j_B) is zero. Again we assume that $N_K(M) dM$ is identical for all the K-blocks in all the j -mers. Then the average composition $\bar{x}_j$, the number- and weight-average molecular weight $\langle M_j \rangle_n$ and $\langle M_j \rangle_w$ can be related with $\bar{M}_n^K$ and $\bar{M}_w^K$ of the precursors by Eqs. (11)–(13). The quantities $\bar{x}$, M_n and M_w of the whole mixture are

$$\bar{x} = \sum w_j \bar{x}_j = M_n^{-1} \sum n_j \bar{x}_j \langle M_j \rangle_n \quad (16a)$$

$$M_n = \sum n_j \langle M_j \rangle_n \quad (16b)$$

$$M_w = \sum w_j \langle M_j \rangle_w \quad (16c)$$

where w_j is the weight fraction of the j -mer in the mixture

$$w_j = n_j \langle M_j \rangle_n / M_n \quad (17)$$

The summation in Eq. (16) extends over all the j -mers including homopolymer contamination. Apparently for a mixed block copolymer the simple relations, Eqs. (11a) and (13a), are invalid. This in turn is an indication of the sample being a mixture but not a pure block copolymer. Anyway, combining these equations with Eqs. (11)–(13), we have

$$M_w^k / M_n^k = 1 + Y_k = \sum n_j k (j_k + \bar{Y}_k) / (\sum n_j j_k)^2 \quad (18)$$

Then Eq. (18) combined with Eq. (14) predicts the values of M_w , P , and Q of the mixed block copolymer. In the above derivations it is clear that only the knowledge of $\bar{x}$, $\bar{Y}_k$, and n_j is enough to estimate the extent of heterogeneity as represented by the parameters M_w/M_n , P/M_w , and Q/M_w . This makes it unnecessary to carry out light scattering measurements for the purpose of the heterogeneity analysis.

The CH- and MWD-function of the j -mer $W_j(x, M)dx dM$ is given by Eq. (10), in which m is replaced by j_A and n by j_B . Then we have for the distribution function of the mixed block copolymer

$$W(x, M)dx dM = \sum w_j W_j(x, M)dx dM \quad (20)$$

Again the knowledge of $N_k(M)dM$ and n_j 's is enough to predict the distribution function. *Examples of mixed block copolymers:* Probably the simplest example of mixed block copolymers is an anionically prepared AB-diblock copolymer under the presence of impurities. The product is a mixture of, say, homopolymer A and AB-diblock copolymer, i.e., $A^* \rightarrow A + AB^*$. Let k be the mole ratio of the deactivated to the whole A-precursors, $k = [A]/[A^*]$. Then we have $n_1 = k(1_A = 1, 1_B = 0)$ and $n_2 = 1 - k(2_A = 2_B = 1)$ and the following simple relations

$$\bar{x} = \bar{M}_n^A / [\bar{M}_n^A + (1 - k)\bar{M}_n^B] \quad (21a)$$

Table I. Relative Amounts and Number Average Molecular Weights of Constituent Species in a Mixed Block Copolymer Prepared by a Dianionic Initiator†

In the precursor			In the product		
Species	Relative moles	$\langle M_j \rangle_n$	Species	Relative moles	$\langle M_j \rangle_n$
A*	2s	$\bar{M}_n^A$	A	2sk	$\bar{M}_n^A$
AA	1-s	$2\bar{M}_n^A$	AA	$(1-s)k^2$	$2\bar{M}_n^A$
			AB	$2s(1-k)$	$\bar{M}_n^A + \bar{M}_n^B$
			AAB	$2(1-s)(1-k)k$	$2\bar{M}_n^A + \bar{M}_n^B$
			BAAB	$(1-s)(1-k)^2$	$2(\bar{M}_n^A + \bar{M}_n^B)$

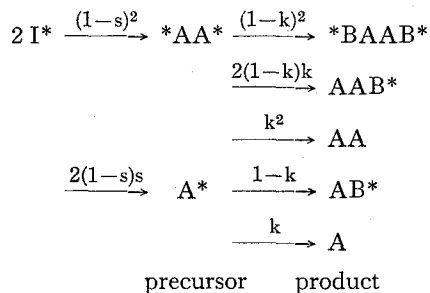
† The parameter s is the mole ratio of the deactivated to the whole initiators, and k the mole ratio of the deactivated to the whole A-terminals.

$$M_w^A/M_n^A = 1 + \bar{Y}_A, \text{ and } M_w^B/M_n^B = (1 + \bar{Y}_B)/(1 - k) \quad (21b, c)$$

$$M_n = \bar{M}_n^A + (1 - k)\bar{M}_n^B \quad (21d)$$

Other quantities also can be calculated easily.

A BAB-triblock copolymer prepared by a dianionic initiator should give a somewhat more complex mixture, if impurities exist in the reaction system. The product is not simply a mixture of poly(A), poly(AB), and poly(BAB), because the reaction would proceed according to the following scheme:



It should be noted that even the precursor has the MWD different from that of the homopolymer contaminant in the product, because the ratio of AA to A is different in the precursor and the product. Incomplete removal of the homopolymer contaminant would complicate the situation. Anyway the values of n_j and $\langle M_j \rangle_n$ will be those listed in Table I.

Commercially important block copolymers of polystyrene-polydiene-polystyrene type, *e.g.*, Kraton from Shell Chemical Company,²²⁾ are prepared by coupling of AB-diblock copolymers. Apparently the product could be a mixture of poly(AB) and poly(BAAB), of which the relative amounts depend on the coupling efficiency.

A multiblock copolymer of polystyrene (PST) and polytetrahydrofuran (polyTHF) prepared by Yamashita *et al.*²⁸⁾ through ion coupling between PST-dianion and polyTHF-dication provides an excellent example of a mixed block copolymer, to which the present theory is applicable. The relative frequencies, the sizes *etc.* of the constituent species can be described by the theory of condensation polymerization developed by Flory.³⁵⁾ In

Table II. Relative Amounts and Number-Average Molecular Weights of Constituent Species in a Mixed Block Copolymer Prepared by Coupling of Dianionic and Dicationic Precursors*.

Species	Relative Moles		$\langle M_j \rangle_n$
	at $p=p$	at $p=1$	
Odd-A j-mer	$p^{j-1}r^{j/2} \frac{(1-p)^2 r^{-1/2}}{1+1/r-2p}$	0	$[(j+1)\bar{M}_n^A + (j-1)\bar{M}_n^B]/2$
Odd-B j-mer	$p^{j-1}r^{j/2} \frac{(1-rp)^2 r^{-3/2}}{1+1/r-2p}$	$r^{j/2}(1-r)^{j-1/2}$	$[(j-1)\bar{M}_n^A + (j+1)\bar{M}_n^B]/2$
Even j-mer	$p^{j-1}r^{j/2} \frac{2(1-p)(1-rp)}{(1+1/r-2p)r}$	0	$(j/2)(\bar{M}_n^A + \bar{M}_n^B)$

* The parameter r is the mole ratio of the A- to B-groups, $r = \bar{N}_A/\bar{N}_B < 1$, initially present in the system. The parameter p is the probability of an A-group reacted, *i. e.*, the extent of reaction of A. Then rp is the extent of reaction of B.

this system three kinds of copolymer molecules can be found; molecules composed of even-number of blocks (even j-mer), molecules composed of odd-number of blocks and having A-blocks at both ends (odd-A j-mer), and molecules composed of odd-number of blocks and having B-blocks at both ends (odd-B j-mer). The values of n_j , and $\langle M_j \rangle_n$ estimated by the Flory theory are listed in Table II. These values and $N_K(M)dM$ may be combined with Eq. (10) to predict the CH- and MWD-function.

Behavior of the Model

Approximation of equal blocks: Although a complete CH- and MWD-function can be deduced from Eq. (10), it is often not practical to carry out the numerical multiple integration in Eq. (10), if the block-number is large. A good way to avoid this difficulty is to employ an approximate expression for the true MWD function, which can be handled analytically. Another possible alternative is to employ an approximation of equal blocks, which assumes that all blocks of the same type in the same molecule are of the same length. This approximation has been introduced by Tung and Wiley²⁹ for the analysis of graft copolymers. For a (m, n)-multiblock copolymer, we use the following equation instead of Eq. (10)

$$W^*(x, M)dx dM = (M^2/mnM_n)N_A(xM/m)N_B[(1-x)M/n]dx dM \quad (22)$$

To test this approximation, we employed the Schulz (number-based) MWD function³⁴ for the precursors

$$N(M)dM = [y^h/I(h)] \{M^{h-1}\exp(-yM)\} dM \quad (23a)$$

$$y = \frac{h}{M_n} = \frac{h+1}{M_w} = \frac{h+2}{M_z} = \dots \quad (23b)$$

Using Eq. (23), we carried out the multiple integration of Eq. (10) and the approximate calculation in Eq. (22). The results are compared in Fig. 1 in the forms of the CH-function $W(x)$, the MWD-function $W(M)$, and the average composition $\langle x \rangle$ at each level of M

$$W(x)dx = \left[\int_0^\infty W(x, M)dM \right] dx \quad (24a)$$

$$W(M)dM = \left[\int_0^1 W(x, M)dx \right] dM \quad (24b)$$

$$\langle x \rangle = W^{-1}(M) \left[\int_0^1 xW(x, M)dx \right] \quad (24c)$$

Apparently the approximation, Eq. (22), is exact for a diblock copolymer. This represents all multiblock copolymers in a class, wherein the overall composition $\bar{x}$ and the number-average molecular weight M_n of the block copolymers are the same, and also the MWD indices of the precursors are the same. Usually the Eq. (22) gives the largest heterogeneity, and the real ones with larger block number are less heterogeneous. This is the result of neglecting the compensating effect in random-coupling mechanism. The approximation is rather poor especially for those with large block number.

Models with Schulz MWD-function: To examine the nature of the random-coupling model in greater detail, we present here some examples of CH- and MWD-function, employing Schulz MWD-function for the precursors. Use of such analytical functions

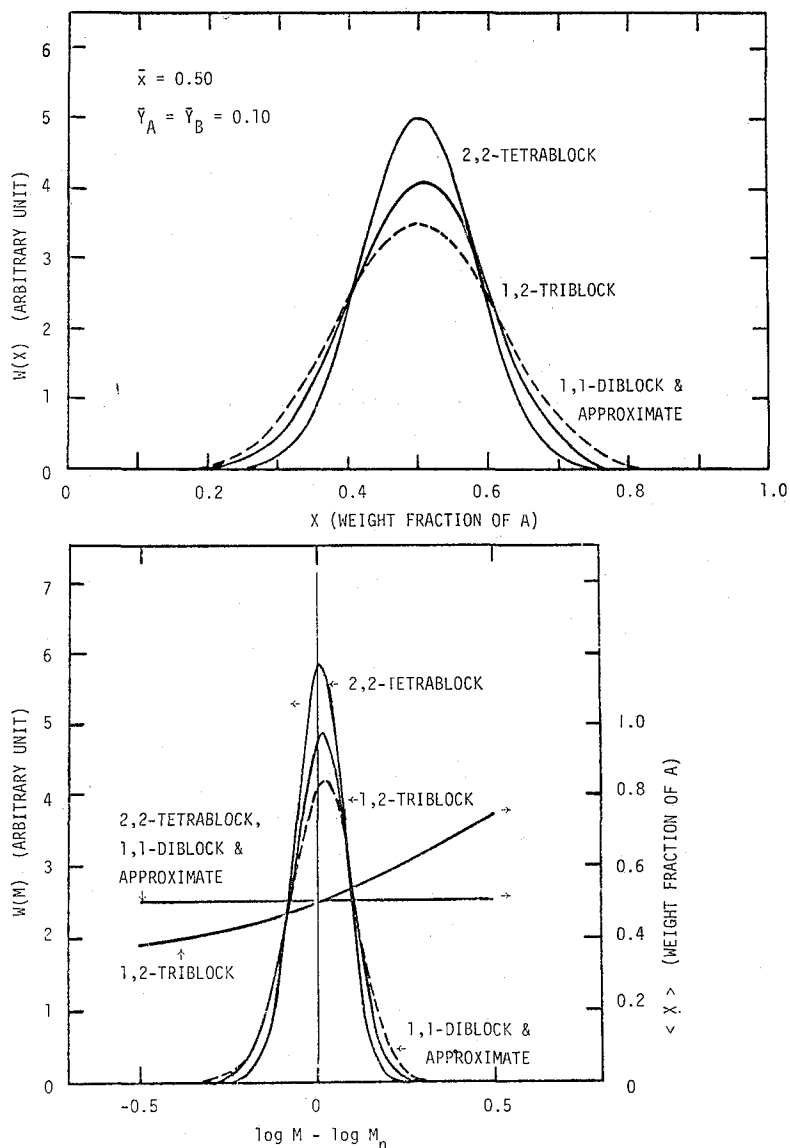


Fig. 1. Test of the approximation of equal blocks for (m, n) -multiblock copolymers with Schulz MWD functions for the precursors, which were assumed to have the MWD indices $\bar{Y}_A = \bar{Y}_B = 0.10$, and overall composition $\bar{x} = 0.50$: From the above, (a) the $W(x)$ versus x relations; and (b) the $W(M)$ versus $\log(M/M_n)$ relations with the variation of composition $\langle x \rangle$. Broken curves indicate the approximation which are exact for (1, 1)-diblock copolymer.

is convenient because of the following reasons: The Schulz MWD-function involves only two adjustable parameters, M_n and M_w/M_n (through y and h in Eq (23)). The values of $\bar{M}_n^k$ s can be related with M_n and $\bar{x}$ of the block copolymer by Eq (11) (by Eq. (16) for a mixed block copolymer). Therefore, the features of block copolymer heterogeneity can be expressed only by the MWD indices $\bar{Y}_A$ and $\bar{Y}_B$ of the precursors, when M_n and $\bar{x}$ have been given.

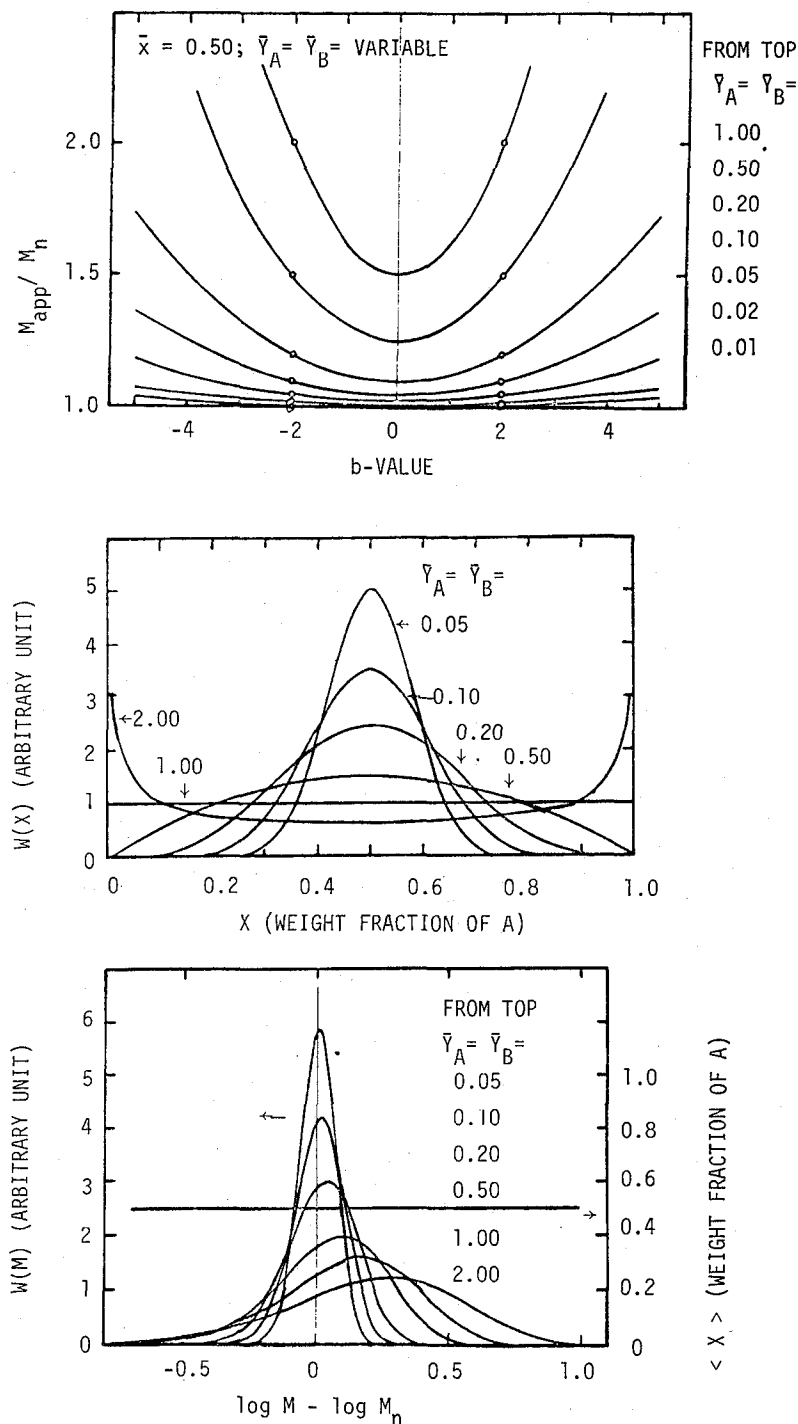


Fig. 2. Typical behavior of model diblock copolymers, for which the parameters were $\bar{x}=0.50$ with varying $\bar{Y}_A=\bar{Y}_B$ as indicated: From above, (a) the M_{app}/M_n versus b relations, in which circles indicate solvents isorefractive to either one of the blocks, *i. e.*, ν_A or $\nu_B=0$; (b) the $W(x)$ versus x relations; and (c) the $W(M)$ and $\langle x \rangle$ versus $\log (M/M_n)$ relations.

Heterogeneities of Block and Graft Copolymers

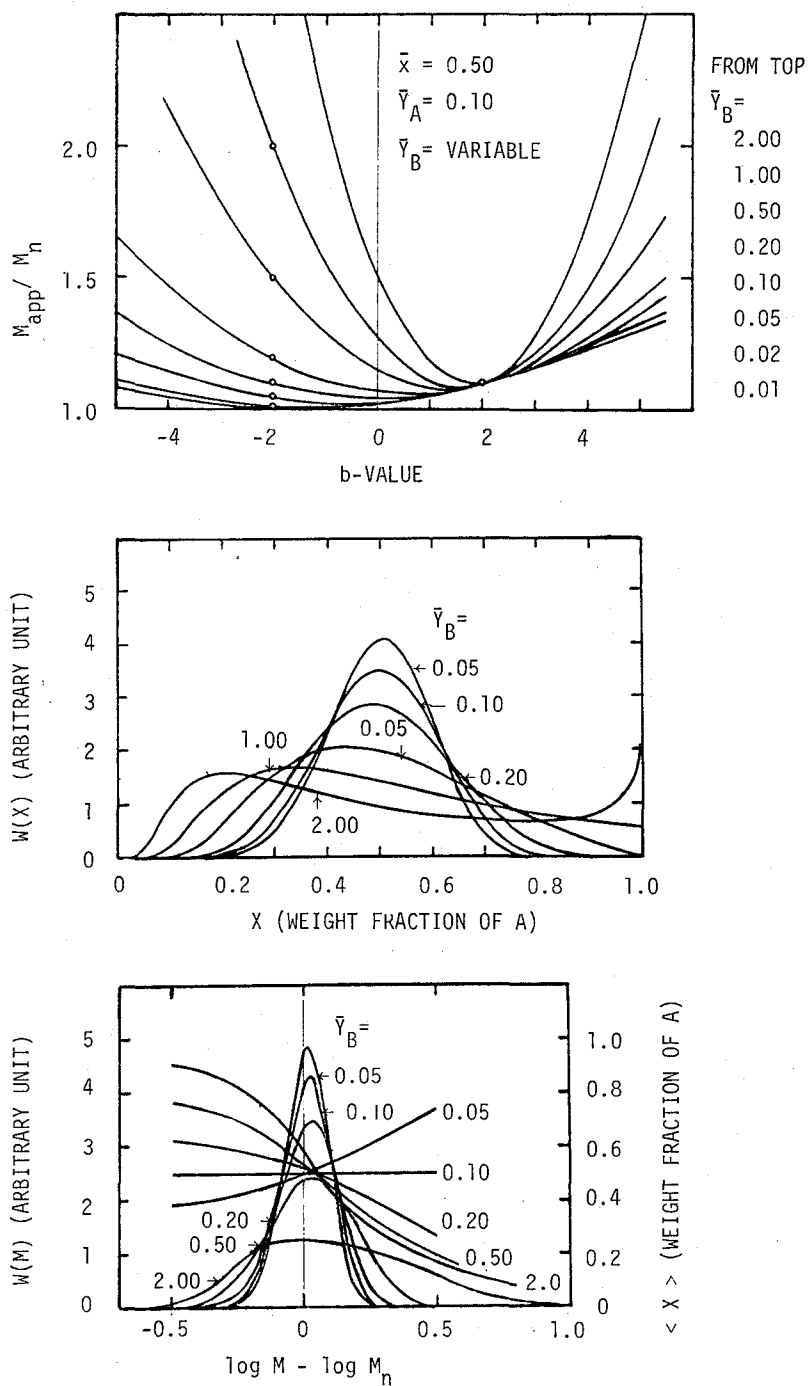


Fig. 3. Typical behavior of model diblock copolymers, for which $\bar{x}=0.50$ and $\bar{V}_A=0.10$ with varying $\bar{V}_B$ as indicated. See caption of Fig. 2.

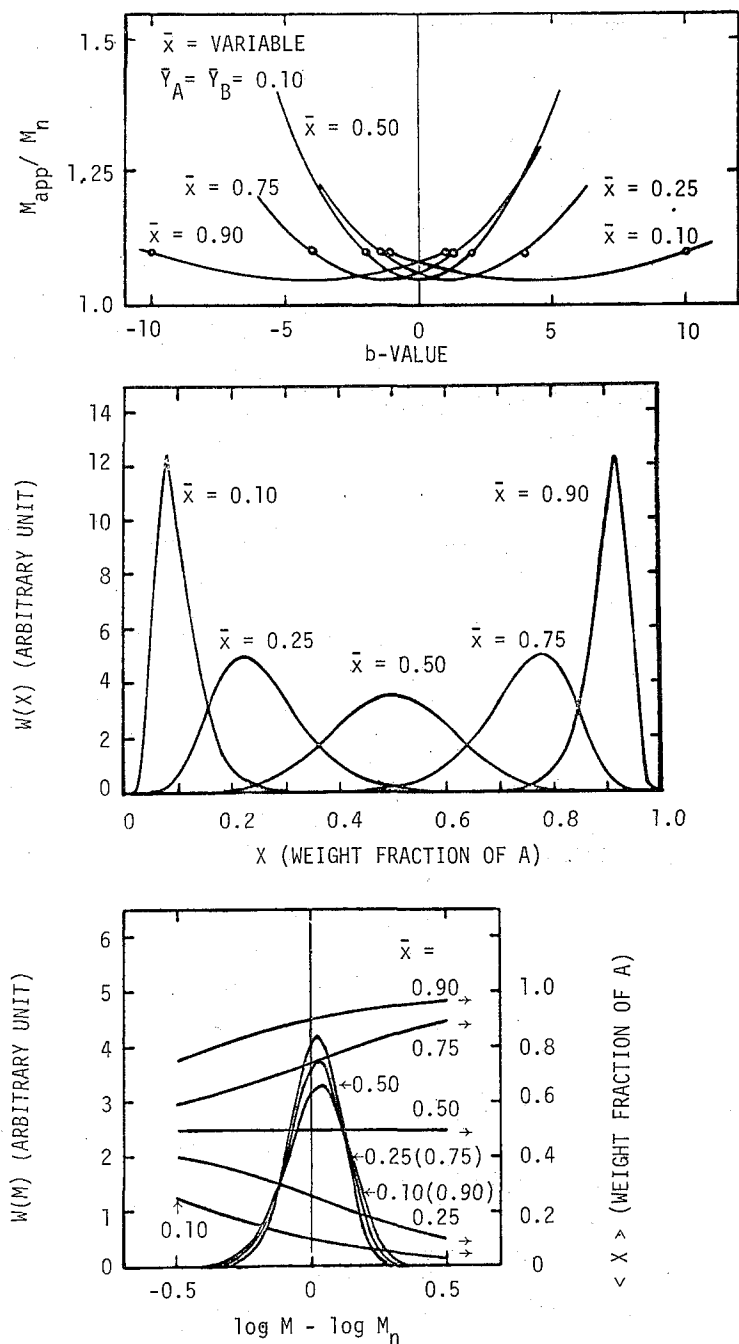


Fig. 4. Typical behavior of model diblock copolymers, for which $\bar{V}_A = \bar{V}_B = 0.10$ with varying $\bar{x}$ as indicated. See caption of Fig. 2.

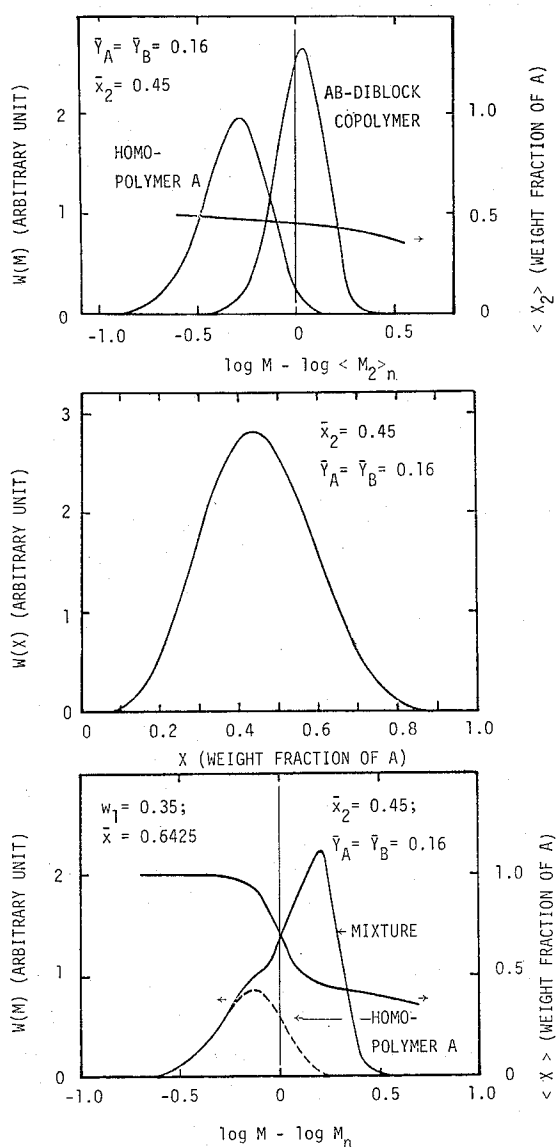


Fig. 5. Typical behavior of a model mixed block copolymer of the type $A^* \rightarrow A + AB$, which approximately represents a mixture of PST and PST-PMMA diblock copolymer shown in Fig. 6: From above, (a) the $W(M)$ and $\langle x_2 \rangle$ versus $\log(M/\langle M_2 \rangle_n)$ relations of poly (A) (=component 1) and poly (AB) (=component 2), for which $\bar{V}_A = \bar{V}_B = 0.16$ and $\bar{x}_2 = 0.45$; (b) the $W_2(x)$ versus x curve for poly (AB); and (c) the $W(M)$ and $\langle x \rangle$ versus $\log(M/M_n)$ relations for a mixture of $w_1 = 0.35$ and $\bar{x} = 0.6425$. Broken curve indicates the contribution of the poly(A) component.

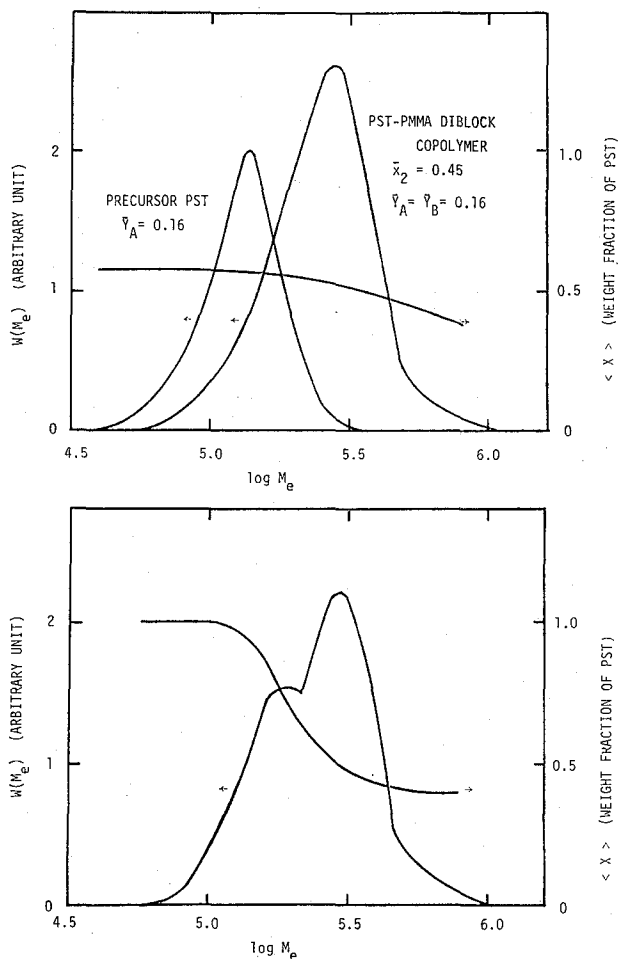


Fig. 6. Results of dual-detector gpc analysis of a mixture of PST and PST-PMMA diblock copolymer: From above, gpc chromatograms, $W(M_e)$ and $\langle x \rangle$ versus $\log M_e$ of PST and PST-PMMA; and (b) those of the mixture. The chromatograms were corrected only for the detector response but not for the elution volume versus molecular weight calibration of the block copolymer.

Below the M_{app} versus b relation (Eq. 14), the $W(x)$ function (Eq. 24a) and the $W(M)$ versus $\log M$ relation (Eq. 24b) are demonstrated for AB-diblock copolymers with the Schulz-MWD-functions for their precursors. Three typical examples are given here in Fig. 2 through 4. They are (i) a set of curves at $\bar{x}=0.50$ with varying $\bar{Y}_A=\bar{Y}_B$; (ii) that at $\bar{x}=0.50$ and $\bar{Y}_A=0.10$ with varying $\bar{Y}_B$; and (iii) that at $\bar{Y}_A=\bar{Y}_B=0.10$ with varying $\bar{x}$.

Some interesting features of the block copolymer heterogeneity emerge from the results. First of all, the compositional heterogeneity is usually considerably large, while the MWD is relatively narrow: For example, even a sample with the value $\bar{Y}_A (= \bar{Y}_B)$ as small as 0.01 has the halfwidth of $x=0.04$ around its peak composition $\bar{x}=0.50$, while its MWD index $Y=0.005$. If the MWD-indices $\bar{Y}_A$ and $\bar{Y}_B$ of the precursors exceed one, the product becomes practically a mixture of homopolymers (*cf.*, Fig. 2). Although this is a direct consequence of using the Schulz function, the situation should be more or

less similar in those of other types of the MWD functions.

The second feature is that, as opposed to statistical copolymer, the light-scattering P parameter is not generally zero. For block copolymer, it becomes zero, if and only if $\bar{x}Y_A = (1-\bar{x})Y_B$ holds. Then as anticipated from Eq. (14b), the composition $\langle x \rangle$ at constant level of M decreases, stays constant, or increases with M according to whether $\bar{x}Y_A$ is smaller, equal to, or larger than $(1-\bar{x})Y_B$, respectively. The $\langle x \rangle$ versus M relation is similar (but not exactly the same) to the $\langle x \rangle$ versus elution volume V_e relation obtained by a dual detector gpc. The invariance of $\langle x \rangle$ with M (or V_e) does not at all guarantee compositional homogeneity of the sample.

Another example is the results of a mixture of an AB-diblock copolymer and its precursor homopolymer A. Figure 5 shows the results, in which the parameters were chosen to represent an actual system of polystyrene (PST)-poly(methyl methacrylate) (PMMA) AB-diblock copolymer and its precursor PST (component A).³⁷ On the other hand, Figure 6 shows dual detector gpc data of the same system. The data are plotted in the form of $W(M_e)$ and $\langle x \rangle$ versus $\log M_e$, where M_e is the gpc apparent molecular weight as determined by a conventional V_e versus M calibration with PST standards.^{18,19,37} These two sets of data are not quite identical with each other, since the gpc chromatograms were corrected only for the difference in the detector response but not for the V_e versus M calibration for PST-PMMA block copolymers.^{37,38} However, we see a qualitative agreement between the theory and the gpc experiments as shown in Figs. 5 and 6.

HETEROGENEITY OF GRAFT COPOLYMERS

Random Grafting Statistics

Definition of the system: Another interesting example of the CH- and MWD-analysis is that of a graft copolymer. We consider here a simplest case in which grafting is completely random and no side reactions such as backbone degradation and cross-linking take place during the reaction. Graft distribution and MWD analysis of such a system has been already carried out by Tung and Wiley.²⁹ Here we attempt to extend their method to include the description of average molecular weights and CH-function.

We consider a product obtained by polymerization of monomer A in the presence of homopolymer B (backbone chains), in which occasional grafting of homopolymer A (graft chains) onto homopolymer B is induced. The following parameters are convenient to describe the system:

$$\text{grafting efficiency } (1-f) = W_A^G / W_A \quad (25a)$$

$$\text{graft ratio } g = W_A^G / W_B \quad (25b)$$

where $W_A = W_A^F + W_A^G$ is the weight of all (free and grafted) A-chains, and W_B is that of B-chains initially added to the polymerization mixture; the superscript G refers to grafted components and F to free or ungrafted components. The grafting probability p for a B-segment (or q for an unit mass of B-segment) to be grafted is the ratio of the total number of graft A-chains N_A^G divided by the total number of B-segments (or the mass of B-chains W_B) in the system. Random grafting states that all B-segments have equal

probability to be grafted. These parameters g , f , and q (or p) may then be related as

$$q = g/\bar{M}_n^A = (W_A/W_B)(1-f)/\bar{M}_n^A \quad (26)$$

where $\bar{M}_n^A$ is the number-average molecular weight of graft A-chains, which are assumed to have the same MWD with free A-chains separable from the system.³⁹⁾

Before characterizing a grafting-reaction product, one often attempts to (or actually does) remove a part or all of ungrafted components in a preparatory scale. For such a purified system we define the average composition $\bar{x}$ by the weight fraction of A. If an unpurified product as a whole is given, we have

$$\bar{x} = g/(1-f+g) \quad (27a)$$

On the other hand, if a system without any free A-chains remaining is given, we have a simple relation

$$\bar{x} = g/(1+g) \quad (27b)$$

For a system from which only a part of free A-chains have been removed, the parameter f in Eq. (27a) loses its original meaning, but may be redefined as a new parameter representing the weight ratio of the residual free A-chains to the all A-chains in the system.

The number-average molecular weight M_n of such a system is, by definition, the total mass divided by the total number of molecules, which is the number of B-chains plus the number of residual free A-chains N_A^F . Then we have

$$M_n^{-1} = \bar{x}f/\bar{M}_n^A + (1-\bar{x})\bar{M}_n^B \quad (28a)$$

where $\bar{M}_n^B$ is the number-average molecular weight of B-chains initially added to the system. On the other hand, if the values of $\bar{M}_n^A$ are different for the graft and the free A-chains, as demonstrated by Taga and Inagaki⁴⁰⁾ for styrene-grafted-cellulose, the $\bar{M}_n^A$ in Eq. (28a) should be that of the free A-chains, while that of Eq. (26) must be that of the graft A-chains. When both are identical, combining Eqs. (26) and (27), we have

$$M_n^{-1} = \bar{x}/\bar{M}_n^A + (1-q\bar{M}_n^B)(1-\bar{x})/\bar{M}_n^B \quad (28b)$$

where $q\bar{M}_n^B$ is, by definition, the number-average graft frequency $\langle m \rangle_n$, *i.e.*, the total number of the graft A-chains divided by the total number of the backbone B-chains.

The parameter f varies from (1—the grafting efficiency) for an unpurified product to zero for a system completely freed from ungrafted A-chains. For the latter, we have

$$M_n = \bar{M}_n^B/(1-\bar{x}) = g\bar{M}_n^B/\bar{x} \quad (28c)$$

These equations provide an indirect method of determining g and hence the grafting probability q (or p) from easily accessible quantities $\bar{x}$, $\bar{M}_n$, $\bar{M}_n^A$, and M_n^B , among which determination of $\bar{M}_n^A$ is the most problematic, though. The parameter g determined by Eq. (28) can be compared with the value of g directly determined by some analytical methods such as fractionation, chromatographic separation, *etc.*

It should be noted here that so far we have not used the assumption of the random grafting. In other words, the Eqs. (25)–(28) should be generally applicable to any systems regardless of the grafting mechanism. Only if some side reactions on backbones (degradation or cross-linking) have been taking place, the quantity $\bar{M}_n^B$ in Eq. (28) is no

longer that of the original B-chains but that of the B-chains after the reaction. It should also be noted that none of the Eqs. (27) and (28) are valid for a system from which a part or all of ungrafted B-chains have been removed. This is because the MWD and the average molecular weights of the ungrafted B-chains should be different from those of the grafted B-chains, as a result that B-chains of different molecular weights should have different opportunities to be grafted. For example, if the random-grafting statistics prevails, the ungrafted B-chains should have lower average molecular weights than the grafted B-chains, since a B-chain should be grafted with a chance proportional to its molecular weight. This is to be contrasted to the random coupling in block copolymerization, in which all precursors of any lengths should have virtually the same chance of coupling.

For estimating M_w and light-scattering apparent value M_{app} , the Eqs. (5)–(8) are still valid. The problem was discussed by Vorlicek and Kratovil.¹⁷⁾ The problem here is how to correlate the quantities M_n^K , M_w^K , and M_w^{AB} in Eqs. (5)–(8) with more easily accessible quantities, *e.g.*, $\bar{M}_n^K$, $\bar{M}_w^K$, *etc.* Because of the nature of the grafting process as discussed above, the analysis of M_w and M_{app} requires some knowledges on the graft distribution. We will discuss this problem later.

The graft distribution, the CH- and MWD-function: The random-grafting statistics has been beautifully formulated by Tung and Wiley,²⁹⁾ which will be briefly summarized below. Reminding that p is the probability of a B-segment to be grafted, we may write the probability P_m^n of a backbone B-chain having n segments to be grafted m times (including $m=0$, *i.e.*, a case in which the chain escaped from grafting):

$$P_m^n = C_m^n p^m (1-p)^{n-m} \quad (29)$$

where C_m^n is the binomial coefficient. For $n \gg m$, Eq. (29) can be approximated by the Poisson distribution

$$P_m^n = (np)^m \exp(-np) / m! \quad (30a)$$

Or recalling that $np=qM$ with M being n time the mass of a B-segment, we have

$$P_m^n = (qM)^m \exp(-qM) / m! \quad (30b)$$

Let $W_B(M)$ represent the normalized MWD of backbone B-chains. The portion of backbones with molecular weight M and grafted m times is

$$W_B^m(M) = P_m^n W_B(M) \quad (31a)$$

Then the weight fraction of backbone B-chains having m -fold grafts is

$$w_B^m = \int_0^\infty W_B^m(M) dM \quad (31b)$$

While the relative number of such chains is

$$N_B^m(M) = M^{-1} W_B^m(M) \quad (31c)$$

$$N_m = N_B^m = \int_0^\infty M^{-1} W_B^m(M) dM \quad (31d)$$

From Eqs. (31a)–(31d), the number-average and the weight-average graft frequencies can

be defined, respectively, as

$$\langle m \rangle_n = \sum_{m=0}^{\text{all}} m N_B^m / N_B = q \bar{M}_n^B \quad (32a)$$

$$\langle m \rangle_w = \sum_{m=0}^{\text{all}} m w_B^m = q \bar{M}_w^B \quad (32b)$$

Thus the analysis of graft-distribution is possible, if the knowledge of grafting probability, Eq. (30), and the MWD of backbone B-chains are available.

Now from the above graft-distribution expression, Eq. (31), and the MWD of graft A-chains, we can derive the CH- and MWD-function for the graft copolymer. First we introduce the relative number of chains having m -fold grafts and $M = M_A + M_B$ with $M_A = xM = M_1 + M_2 + \dots + M_m$ as

$$\begin{aligned} N_m(M_B, M_1, M_2, \dots, M_m) dM_B dM_1 dM_2 \dots dM_m \\ = N_B^m(M_B) dM_B \prod_{i=1}^m N_A(M_i) dM_i \end{aligned} \quad (33a)$$

where $N_A(M)$ is the normalized number-based MWD of the graft A-chains. The relative weight of chains specified by graft frequency m , composition $x = M_A/M$ and molecular weight M is obtained from Eq. (33a) as

$$\begin{aligned} W_m(x, M) dx dM = M^2 \left\{ N_B^m[(1-x)M] \int^{xM} N_A(M_1) dM_1 \dots \right. \\ \left. \dots \int^{M-M_1 \dots - M_{m-2}} N_A(M_{m-1}) N_A(xM - M_1 \dots - M_{m-1}) dM_{m-1} \right\} dx dM \end{aligned} \quad (33b)$$

Adding up all these components including residual free A-chains, we have the normalized (weight based) CH- and MWD-function as

$$W(x, M) dx dM = \{ \bar{x} f W_A^f(M) \delta(x=1) + [1 - \bar{x} f] W^g(x, M) \} dx dM \quad (34a)$$

$$W^g(x, M) dx dM = (W^g)^{-1} \sum_{m=0}^{\text{all}} W_m(x, M) dx dM \quad (34b)$$

$$W^g = W_A^g + W_B = \sum_{m=0}^{\text{all}} \int_0^\infty \int_0^1 W_m(x, M) dx dM \quad (34c)$$

Here $W^g(x, M) dx dM$ is the normalized CH- and MWD-function of the graft components including the ungrafted backbones, *i.e.*, the distribution function expected to be obtained when the system is completely freed from residual free A-chains ($f=0$); W^g is the total weight of the graft components; $W_A^f(M)$ is the MWD of free A-chains, which is assumed to be equal to that of the graft A-chains; and $\delta(x)$ is the delta function. When a part or all of ungrafted backbone B-chains have been completely extracted from the system, the function $W^g(x, M)$ and W^g must be modified accordingly: Namely the summation in Eqs. (34b) and (c) should start at $m=1$ and $W_B^0(M)$ term for the residual ungrafted backbones should be added. It should be noted that even in such a case the $W_B(M)$ term in $W_m(x, M)$ must be the one for the original B-homopolymers and not the one for the B-chains after the extraction, since $W_B(M)$ and $W_B^0(M)$ differ from each other (*cf.*, Eqs. (30)–(33)).

Average molecular weights: Now we are ready to derive expressions for various average molecular weights. The number-average M_n has been already given by Eq. (28), which should be valid for any graft copolymer products. For M_w and M_{app} , we have to calculate M_w^K ($K=A$ or B) and M_w^{AB} as defined by Eq. (5). First for M_w^B , noting that $(1-x)M=M_B$ and

$$W_B^{-1} \int_0^1 (1-x)W(x, M)dx dM = W_B(M_B) dM_B$$

we have from Eqs (5d), (31), (33), and (34)

$$M_w^B = \bar{M}_w^B \quad (35a)$$

This implies that the value of M_w^B determined from M_{app} data obtained in a solvent $\nu_A=0$ should be equal to $\bar{M}_w^B$ of the B-chains initially added to the system, if and only if neither the backbone degradation nor the cross-linking take place during the grafting reaction.

Calculation of M_w^A is more complicated. We split the M_w^A term derived from Eqs. (5c), (33), and (34) into the components, one representing free A-chains and each of those representing m -fold grafted chains. Recalling Eq. (33a), we have

$$M_w^A = f \bar{M}_w^A + \sum_{m=1}^{\infty} (W_A^m / W_A) \frac{\int_0^{\infty} \int_0^1 (xM)^2 N_m(x, M) dx dM}{\int_0^{\infty} \int_0^1 (xM) N_m(x, M) dx dM}$$

where W_A^m is the relative weight of graft A-chains in the component having m -fold grafts. The integrals in the above equation become $\bar{M}_w^A + (m-1)\bar{M}_n^A$ (cf., Eq. (11)). Then from Eqs. (31)–(33) and the above equation we have

$$M_w^A = \bar{M}_w^A + (1-f) \langle m \rangle_w \bar{M}_n^A = \bar{M}_w^A + (1-f)g \bar{M}_w^B \quad (35b)$$

Finally for M_w^{AB} , we have from Eqs. (5e) and (31)–(34)

$$M_w^{AB} = (1-\bar{x}) \langle m \rangle_w \bar{M}_n^A = (1-\bar{x})g \bar{M}_w^B \quad (35c)$$

Now combining Eq. (35) with Eqs. (5) and (8), we have for M_{app}

$$M_w = \bar{x} \bar{M}_w^A + (1-\bar{x}) \bar{M}_w^B + [2-\bar{x}(1+f)]g \bar{M}_w^B \quad (36a)$$

$$P = \bar{x}(1-\bar{x})(\bar{M}_w^A - \bar{M}_w^B) + (1-\bar{x})[1-\bar{x}(1+f)]g \bar{M}_w^B \quad (36b)$$

$$Q = \bar{x}(1-\bar{x})[(1-\bar{x})\bar{M}_w^A + \bar{x}\bar{M}_w^B - (1-\bar{x})(1+f)g \bar{M}_w^B] \quad (36c)$$

It should be noted that if the average molecular weights of the graft and free A-chains differ from each other, the $\bar{M}_w^A$ term in Eqs. (35) and (36) should be the weight average of the two different values of $\bar{M}_w^A$. If all the free A-chains are extracted from the system, i.e., $f=0$ and $g=\bar{x}/(1-\bar{x})$, the molecular weight values should be those of the graft A-chains, and then Eqs. (28) and (36) become very simple. On the other hand, if a part or all of the ungrafted B-chains are extracted from the system, the $\bar{M}_w^B$ term is not equal to that of the original B-chains but should be a complicated average calculated by using the adequately modified MWD function as mentioned above.

Using Eq. (33), we also can write down the average composition $\bar{x}_m$ and the number-average molecular weight $\langle M^m \rangle_n$ (and other averages also) of the chains having m -fold grafts as follows:

$$\bar{x}_m = m\bar{M}_n^A / \langle M^m \rangle_n \quad (37a)$$

$$\langle M^m \rangle_n = \langle M_B^m \rangle_n + m\bar{M}_n^A \quad (37b)$$

Here $\langle M_B^m \rangle_n$ is the number-average molecular weight of backbones that are grafted m times. Likewise using Eq. (31), we can define the number-average $\langle M_B^m \rangle_n$ and other averages of the backbones having m -fold grafts as

$$\langle M_B^m \rangle_n = \int_0^\infty W_B^m(M) dM / \int_0^\infty M^{-1} W_B^m(M) dM \quad (37b)$$

$$\langle M_B^m \rangle_w = \int_0^\infty M W_B^m(M) dM / \int_0^\infty W_B^m(M) dM \quad (37c)$$

.....

$$\langle M_B^m \rangle_n = \langle M_B^{m-1} \rangle_w = \langle M_B^{m-2} \rangle_z = \dots \quad (37d)$$

Apparently in each average the values with different m differ from one another and also from $\bar{M}_n^B$, unless the original B-chains are monodisperse in molecular weight and no side-reaction of the backbones occur.

Behavior of Random Grafting Model

Approximation of equal grafts: Because of the time-consuming nature of the multiple integration in Eq. (33), Tung and Wiley²⁹ adopted the approximation of equal grafts, which states that all graft A-chains in a molecule have the same length. Use of this approximation replaces Eq. (33) by

$$W^*(x, M) dx dM = (M^2/m) N_B^m [(1-x)M] N_A (xM/m) dx dM \quad (38)$$

Tung and Wiley²⁹ tested this approximation for the MWD function of graft copolymer chains with $m=2$, and found it to be fairly good approximation. We also have tested this approximation for a system to which the Schulz MWD-function is applicable. The situation is similar to the case of a multiblock copolymer: Namely a graft copolymer component with m -fold grafts is similar to a $(m, 1)$ -multiblock copolymer with $N_A(M)$ and $N_B^m(M)$ instead of $N_B(M)$ for the MWD-function. Therefore, the approximation predicts a larger heterogeneity for the component having larger m . However, in this case the approximation is somewhat better by the following two reasons. One is that, as mentioned before, in a graft copolymer backbones having larger M_B are more frequently grafted, as opposed to a block copolymer in which all chains of any lengths have virtually equal opportunity of coupling. This would suppress, to some extent, the discrepancy between the results of the exact and approximate models. Secondly, the relative amount of a graft component having larger m decreases very rapidly as m increases, unless the grafting probability is very high (cf., Table III). Therefore, the contribution of the poorly approximated component becomes negligibly small. This is not necessarily so in a mixed multiblock copolymer.

Heterogeneities of Block and Graft Copolymers

Table III. Typical Graft-Distributions of Randomly Grafted Polymers Having Backbones with Varying Polydispersity under the Same Grafting-Probability*.

Graft Number m	Weight Fraction of Backbones Grafted m Times w_B^m					
M_w^B/M_n^B	1.00	1.05	1.10	1.50	2.00	3.00
0	0.741	0.732	0.722	0.656	0.5917	0.4941
1	0.222	0.227	0.232	0.257	0.2731	0.2779
2	0.033 ₃	0.036 ₉	0.040 ₅	0.067 ₁	0.0945	0.1303
3	0.003 ₃	0.004 ₂	0.005 ₁	0.014 ₆	0.0291	0.0570
4	0.000 ₂	0.000 ₄	0.000 ₅	0.002 ₉	0.0084	0.0241
5				0.000 ₅	0.0023	0.0099
6				0.000 ₁	0.0006	0.0040
7					0.0002	0.0016
8					0.0000 ₄	0.0007
9						0.0003
10						0.0001

* The grafting probability was assumed to be $q\bar{M}_n^B=0.300$.

Graft-distribution in model system: Graft-distribution may be deduced from the knowledges of q (or p) and the MWD of B-homopolymer initially added to the system, provided the random-grafting statistics prevails. We will demonstrate a few examples, again using the Schulz MWD-function for $W_B(M)$. Table III summarizes typical graft-distributions of backbones having different MWD indices onto which the grafting takes place with the same probability q . Apparently the narrower becomes the MWD of backbones, the more rapidly decreases the contribution of components with large m . Table IV summarizes the results of random-grafting on backbones of a given MWD index with different probabilities. The most densely populated species is that having $m=\langle m \rangle_n$. In heavily grafted systems (*e.g.*, those with $\langle m \rangle_n > 1$), the population of highly grafted species is considerably large and its decrease with increasing m is very slow, especially for systems having highly polydisperse backbones.

For the same model we can calculate various average molecular weights of backbones having $m=1, 2, 3, \dots$ grafts by using Eqs. (23), (31), and (37):

$$1 + \frac{\langle m \rangle_n}{h_B} = \frac{\bar{M}_n^B}{\langle M_B^0 \rangle_n} = \frac{\bar{M}_w^B}{\langle M_B^1 \rangle_n} = \frac{\bar{M}_z^B}{\langle M_B^2 \rangle_n} = \dots \quad (39)$$

Interestingly the ratios of $\langle M_B^0 \rangle_n$ of ungrafted backbones to those with one, two, three *etc.* grafts are equal, respectively, to the ratios of $\bar{M}_n^B$ to $\bar{M}_w^B$, $\bar{M}_z^B$, *etc.* of the original backbone chains. The ratio $\langle M_B^m \rangle_w / \langle M_B^m \rangle_n$ for any value of m is equal to $\bar{M}_w^B / \bar{M}_n^B$. These relations would be generally valid for other systems having different types of MWD-function. In fact Ikada *et al.*^{(23), (29)} found that $\langle M_B^1 \rangle_n / \langle M_B^0 \rangle_n = 2$ for many systems which are presumably approximated by the most probable distribution, *i.e.*, $\bar{M}_w^B / \bar{M}_n^B = 2$. Their results are a special case of Eq. (39).

Heterogeneity of model graft copolymer: To examine the nature of the random-grafting model, we present here an example of CH- and MWD-function of a model system, again employing the Schulz MWD-function for the A- and B-chains. Figure 7 shows the results, wherein the parameters chosen were $\bar{x}=0.600$ and $g=0.200$; $10^{-3}\bar{M}_n^A=66.7$ and $\bar{Y}_A=$

Table IV. Typical Graft-Distributions of Randomly Grafted Polymers under Varying Grafting-Probability*.

Graft Number m	Weight Fraction of Backbones Grafted m Times w_B^m					
$q\bar{M}_n^B$	0.100	0.200	0.300	0.600	1.200	3.000
0	0.761	0.604	0.494	0.306	0.1595	0.0540
1	0.190	0.259	0.278	0.251	0.1689	0.0694
2	0.040	0.092	0.130	0.171	0.1490	0.0744
3	0.008	0.031	0.057	0.109	0.1227	0.0744
4	0.001	0.010	0.024	0.067	0.0975	0.0717
5	0.000 ₃	0.003	0.010	0.040	0.0757	0.0676
6		0.001	0.004	0.024	0.0579	0.0628
7		0.000 ₃	0.002	0.014	0.0438	0.0577
8			0.000 ₇	0.008	0.0328	0.0525
9				0.005	0.0244	0.0475
10				0.003	0.0181	0.0428
15				0.000 ₂	0.0038	0.0240
20					0.0008	0.0127
25					0.0002	0.0066
30					0.0000 ₃	0.0033
35						0.0017
40						0.0008
45						0.0004
50						0.0002

* The backbone polydispersity was assumed to be $\bar{M}_w^B/\bar{M}_n^B=3.00$.

1.00; and $10^{-3}\bar{M}_n^B=100$ and $\bar{Y}_B=2.00$. These values lead to $f=0.8667$ and $\langle m \rangle_n=0.300$. The model approximately represents an unpurified styrene-grafted-polybutadiene obtained by benzoyl peroxide initiated polymerization of styrene under the presence of a polybutadiene prepolymer.⁴¹⁾ Certain interesting features emerge from the results. First of all, the system seems to be a mixture of two homopolymers and relatively low A-containing copolymer. This is due to the relatively low grafting-efficiency and the low $\bar{M}_n^A$ value of this particular system. Note that, for example, $\bar{x}_1=0.2623$. Secondly, in the CH-function the component with only one graft shows a peculiar composition dependence. This is due to the high heterogeneity of the A-chains and the relatively low value of $\bar{x}_1$. Namely since the polydisperse A-chains have large number of low molecular weight species, the backbones are more easily grafted with these smaller A-chains. The situation is similar to a diblock copolymer composed of highly polydisperse precursors (cf., Figures 2 and 3).

On the other hand, Figure 8 shows a gpc chromatogram, $W(M_e)$ versus M_e data, of the same graft product obtained by a dual detector gpc.^{37,41)} Here M_e is determined from the elution volume V_e versus M calibration with PST standards and is not corrected for the calibration of the graft copolymer. Nevertheless, the qualitative behavior of these two results appear to be fair agreement. Tung and Wiley²⁹⁾ have made a more direct comparison of theoretical and experimental chromatograms of a styrene-grafted-polybutadiene system, after theoretically correcting the V_e versus M relation and the refractom-

Heterogeneities of Block and Graft Copolymers

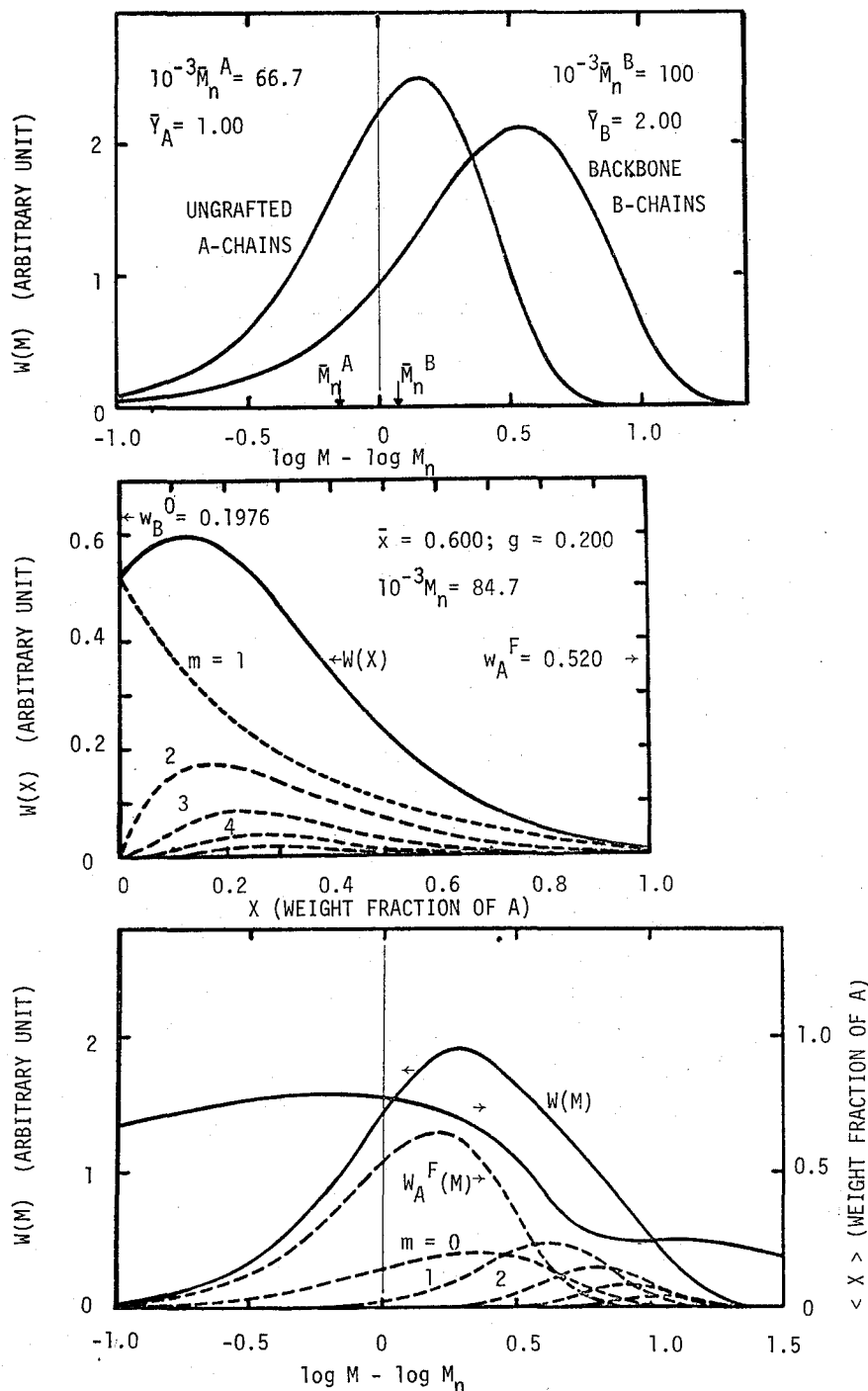


Fig. 7. Typical behavior of a random-grafting model, for which the parameters chosen were $\bar{x}=0.60$ and $g=0.20$; $10^{-3} \bar{M}_n^A=66.7$ and $\bar{Y}_A=1.00$; and $10^{-3} \bar{M}_n^B=100$ and $\bar{Y}_B=2.00$. These values lead to $10^{-3} \bar{M}_n=84.7$, $f=0.8667$ and $\langle m \rangle_n=0.300$. The model approximately represents a styrene-grafted-poly-butadiene system shown in Fig. 8. From above, (a) the $W(M)$ versus $\log(M/\bar{M}_n)$ for the graft A-chains and the backbone B-chains; (b) the $W(x)$ versus x relation of the graft system; and (c) the $W(M)$ and $\langle x \rangle$ versus $\log(M/\bar{M}_n)$ relations. Broken curves indicate the contribution of each component as specified.

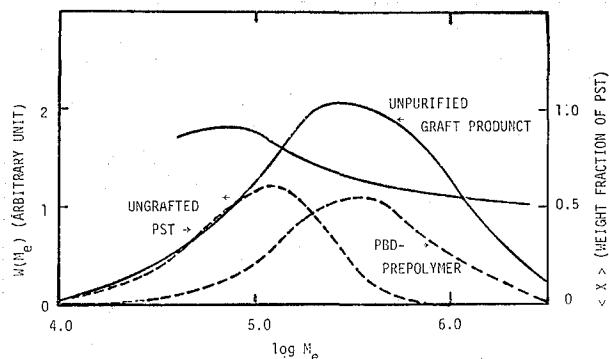


Fig. 8. Dual detector gpc chromatograms, $W(M_e)$ and $\langle x \rangle$ versus $\log M_e$ of an unpurified styrene-grafted-polybutadiene system: Broken curves indicate those of extracted free PST and polybutadiene prepolymer. They were corrected only for the detector response.

eter responses of the graft copolymer. They found a good agreement and concluded that the random-grafting statistics applies quite well to the system they have studied.

Here we have extended the same theory to include the description of various average molecular weights and also the CH-function, which would add several important criteria on checking the heterogeneity of graft copolymers.

CONCLUSION

A theory has been developed to describe various average molecular weights and the CH- and MWD-functions of block and graft copolymers which can be obtained through certain simple reaction mechanisms. For block copolymers, we assume random-coupling mechanism through active terminal groups of the two precursor homopolymers. The knowledges of (i) the type of the polymer obtained (*e.g.*, block number, AB- or BAB-type, *etc.*), (ii) the overall chemical composition, and (iii) the MWD indices $\bar{Y}_A$ and $\bar{Y}_B$ of the precursors suffice to predict the light-scattering apparent versus the number-average value, M_{app}/M_n . If the material is a mixed block copolymer, the knowledge of (iv) the relative amount of each species is required, which may be deduced from the copolymerization kinetics. A complete CH- and MWD-function of such a system can be predicted from the knowledges of (v) the MWD-functions of the precursors in addition to those of (i), (ii), and (iv).

For graft copolymers, we assumed random-grafting mechanism without accompanying any side-reactions such as backbone degradation and cross-linking. Determination of the true graft ratio (or the grafting efficiency) and the number-average molecular weight of the graft side-chains is indispensable for estimating the grafting probability, which is a key parameter in describing the graft-distribution. On the other hand, determination of the overall composition, the number-average molecular weights of the whole system and of the A- and B-chains provides another possible route of estimating the grafting efficiency.

Various average molecular weights including light-scattering apparent value can be related with more easily accessible quantities, as in the case of block copolymers. A

complete CH- and MWD-function of a graft copolymer can be predicted from the knowledges of (i) the overall composition, (ii) the true graft ratio, and (iii) the MWD-functions of the backbone prepolymer and the graft side-chains. Even when the MWDs of the grafted and free side-chains are different, the analysis is still possible, provided these two MWDs are known.

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REFERENCES

- (1) T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944).
- (2) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
- (3) F. T. Wall, *ibid.*, **63**, 1862 (1941); *ibid.*, **66**, 2050 (1944).
- (4) For review, see for example, F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950); G. E. Ham, editor, "Copolymerization," Interscience, New York, 1964.
- (5) R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).
- (6) W. H. Stockmayer, *ibid.*, **13**, 199 (1945).
- (7) I. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).
- (8) O. Fuchs, *Verh.-Ber. Kolloid-Ges.*, **18**, 75 (1958).
- (9) S. Teramachi, H. Nakashima, M. Nagasawa, and I. Kagawa, *Kôgyô-kagaku-Zasshi*, **70**, 1557 (1967).
- (10) S. Teramachi and Y. Kato, *Macromolecules*, **4**, 54 (1971).
- (11) H. Inagaki, H. Matsuda, and F. Kamiyama, *ibid.*, **1**, 520 (1968).
- (12) F. A. Bovey, *J. Polym. Sci.*, **62**, 197 (1962); A. Nishioka, Y. Kato, and N. Ashikari, *J. Polym. Sci.*, **62**, S10 (1962).
- (13) See, for example, U. Johnson, *Ber. Bunsenges. Physik. Chem.*, **70**, 320 (1966).
- (14) See, for example, A. M. Liquori, G. Anzuino, M. D'Alagni, V. Vitagliano, and L. Constantino, *J. Polym. Sci.*, **A2-6**, 509 (1968); T. Saegusa, T. Yatsu, S. Miyaji, and H. Fujii, *Polym. J.*, **1**, 7 (1970); T. Miyamoto and H. Inagaki, *ibid.*, **1**, 46 (1970).
- (15) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).
- (16) W. Bushuk and H. Benoit, *Can. J. Chem.*, **36**, 1616 (1958); M. Leng and H. Benoit, *J. Polym. Sci.*, **57**, 263 (1962); H. Benoit and D. Froelich, in M. B. Huglin, editor, "Light Scattering from Polymer Solution," Academic Press, London, 1972, Chapter 11.
- (17) J. Vorlicek and P. Kratochvil, *J. Polym. Sci., (Phys.)* **11**, 855, 1251 (1973).
- (18) J. C. Moore, *J. Polym. Sci.*, **A2**, 835 (1964); J. F. Johnson and R. S. Porter, editors, "Analytical Gel Permeation Chromatography," (*J. Polym. Sci.*, **C21**), Interscience, New York, 1968.
- (19) J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, *J. Appl. Polym. Sci.*, **13**, 2359 (1969).
- (20) See, for example, J. J. Hermans and H. A. Ende, in B. Ke, editor, "Newer Methods of Polymer Characterization," John Wiley, New York, 1964, Chapter 13.
- (21) See, for example, R. J. Ceresa, "Block and Graft Copolymers," Butterworth, London, 1962; H. A. J. Battaerd and G. W. Tregear, "Graft Copolymers," Interscience, New York, 1967.
- (22) R. Zelinski and C. W. Childers, *Rubber Chem. Tech.*, **41**, 161 (1968); L. J. Fetters, *J. Polym. Sci.*, **C26**, 1 (1969); G. Holden, E. T. Bishop, and N. R. Legge, *ibid.*, **C26**, 37 (1969); G. Holden, *J. Elastoplastics*, **2**, 234 (1970).
- (23) G. E. Molau, in D. McIntyre, editor, "Characterization of Macromolecular Structure," National Research Council, Washington, D. C., 1968; I. Sakurada, Y. Ikada, H. Uehara, Y. Nishizaki,

- and F. Horii, *Makromol. Chem.*, **139**, 183 (1970); Y. Ikada, F. Horii, and I. Sakurada, *J. Polym. Sci. (Chem.)*, **11**, 27 (1973); F. Horii, Y. Ikada, and I. Sakurada, *ibid.*, **11**, 39 (1973).
- (24) F. Kamiyama, H. Inagaki, and T. Kotaka, *Polym. J.*, **3**, 470 (1972).
- (25) T. Uda and T. Tanaka, unpublished experiments.
- (26) M. Szwarc, *Nature*, **178**, 1168 (1956); M. Szwarc, M. Levy, and R. Milkovitch, *J. Amer. Chem. Soc.*, **78**, 2656 (1956).
- (27) M. Szwarc and A. Rembaum, *J. Polym. Sci.*, **22**, 189 (1956); M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," John Wiley, New York, 1968.
- (28) Y. Yamashita, K. Nobutoki, Y. Nakamura, and M. Hirota, *Macromolecules*, **4**, 548 (1971).
- (29) L. H. Tung and R. M. Wiley, *J. Polym. Sci. (Phys.)*, **11**, 1413 (1973).
- (30) D. Freyss, P. Rempp, and H. Benoit, *ibid.*, **B2**, 217 (1969).
- (31) H. Ohnuma, T. Kotaka, and H. Inagaki, *Polymer*, **10**, 501 (1969).
- (32) T. Kotaka, N. Donkai, and H. Inagaki, *J. Polym. Sci.*, **A2-9**, 1379 (1971); N. Donkai and T. Kotaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 201 (1971).
- (33) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093, 1099 (1948).
- (34) G. V. Schulz, *Z. Physik. Chem.*, **B43**, 25 (1939).
- (35) P. J. Flory, *J. Amer. Chem. Soc.*, **58**, 1877 (1936); P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953.
- (36) See, for example, A. Chapiro, editor, "Radiation Chemistry of Polymeric Systems," Interscience, New York, 1962.
- (37) N. Donkai and T. Kotaka, unpublished experiments.
- (38) See, for example, D. N. Cramond, J. M. Hammond, and J. R. Urwin, *Eur. Polym. J.*, **4**, 457 (1968); F. S. C. Chang, *J. Chromatogr.*, **55**, 67 (1971); N. Ho-Duc and J. Prud'homme, *Macromolecules*, **6**, 472 (1973).
- (39) Y. Ikada, personal communication, 1973; Y. Ikada, F. Horii, and I. Sakurada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 6 (1971).
- (40) T. Taga and H. Inagaki, *Angew. Makromol. Chem.*, **33**, 129 (1973).
- (41) T. I. Min, N. Donkai, and T. Kotaka, unpublished experiments.