Size Exclusion Chromatography of Polymers With Random Tetrafunctional Branching

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SIZE EXCLUSION CHROMATOGRAPHY OF POLYMERS WITH RANDOM TETRAFUNCTIONAL BRANCHING*

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ABSTRACT

The behaviour of polydisperse branched copolymers of methyl methacrylate with a small amount of randomly situated tetrafunctional ethylenedimethacrylate units was investigated by means of size exclusion chromatography (SEC). A procedure has been suggested for the conversion of apparent values of molecular parameters of real polymer branched systems ($M_{n,app}$; $M_{w,app}$ obtained from SEC data by calibration of the separation system using a linear polymer) into actual values. This was made possible by off-line coupling of SEC and viscometry. The branching was characterized by the weight average number of branching sites in the macromolecule, m_w, and the branching index, γ.

INTRODUCTION

Separation of polymer molecules in size exclusion chromatography (SEC) is controlled by the size of the hydrodynamic volume of the polymer coil (1,2). By universal calibration for the given column system, solvent and temperature we understand the dependence $\log[\eta]M = f(V)$, which holds irrespective of the topological structure of polymer molecules ([η] is intrinsic viscosity, M is molecular weight, V is elution volume). Due to the dependence of [η] on M (Mark-Houwink equation) for linear macromolecules, their separation in SEC is determined by differences in molecular weights, while randomly branched chains are separated according to differences in their hydrodynamic volume. The number of branch units increases continuously with the chain length, which reduces $[\eta]$ correspondingly (3). Then, with $M_b = M_l$, branched (b) macromolecules are eluated later than linear ones (l); generally, it may be expected that at a certain elution volume chains of the same hydrodynamic volume, but with different M will be eluated. In order to obtain molecular weight distribution (MWD) of a polymer with long branches (LCB), it is suitable to combine SEC with direct detection of viscosity or light scattering. Today, LCB are commonly analyzed also by so-called indirect methods ("off-line coupling"), as this is the case with some commercial polymers, where the trifunctional branch units arise by the chain transfer to polymer. For these cases, several procedures for the conversion of chromatographic data to the actual MWD and parameters characterizing LCB have already been suggested (4-6).

The behaviour of randomly branched polydisperse polymers with tetrafunctional branch units in the

separation by using SEC has been quantitatively pre-
dicted by Shultz (7,8), who also suggested a very
simple and not very time-consuming method of evaluation
of molecular parameters from chromatographic data. The
method consists in the correction of apparent para-
meters which are a result of the application of a tra-
ditional procedure in the evaluation of SEC data for
linear polymers. The ratios between the apparent mole-
cular weight averages (M_n - number and M_w - weight) and
the real ones were calculated using the following as-
sumptions (7):

(1) The primary molecular weight distribution is the
Schultz-Zimm one (distribution of a product polymerized
under the same conditions, but without the possibility
of random branching). The distribution is modified
(broadened) by random intermolecular branching ac-
cording to Stockmayer´s model (9).

(2) The Zimm-Kilb approximation (10) for the intrinsic
viscosity of branched chains is valid,

$$[\eta]_b = K \, g´ M^a \, , \qquad\qquad (1)$$

where for viscosity depression we have $g´ = g^{0.5}$, and
$g = R_b^2 / R_1^2$ is depression of the radius of gyration.

(3) $g_\theta´ = g´$, i.e., the value of viscosity depression is
independent of the magnitude of the exponent of the
Mark-Houwink equation in the solvent used (11).

The model of the branched system considered in
this study can be approximately materialized, e.g.,
by the radical copolymerization of a vinyl monomer with
a divinyl monomer. Experimentally, copolymers of methyl
methacrylate with a small amount of ethylenedimeth-
acrylate were used. Our earlier findings (12,13) indi-
cate that macrorings (if any) present in these copoly-
mers will somewhat modify the assumed elution in SEC

(7). We characterized the poly(methyl methacrylates)
(PMMA) used in this study on the basis of some of
Shultz's predictions; the results of our investigation
are reported below.

MATERIALS AND METHODS

Sample preparation

All samples were prepared by bulk or solution
radical copolymerization of methyl methacrylate (MMA)
with ethylenedimethacrylate (EMA) initiated with 2,2'-
azobis(isobutyronitrile) (AIBN) at 45°C. In this way,
two series of copolymers were prepared (M and MH, cf.
Table 1); samples in the individual series differed
from each other in the degree of conversion or in the
degree of branching).

Methods of measurement

SEC was carried out using an apparatus constructed
at this Institute, with an R-403 flow differential
refractometer (Waters) used for detection. Four separ-
ation columns of standard size, 8x1200 mm, were packed

TABLE 1

Composition of Reaction Mixtures of the Individual
Methyl(methacrylate) (MMA/EMA) Copolymer Series at 25°C

Designation of copolymer	c_{MMA} mol.1^{-1}	c_{EMA} mol.1^{-1}	c_{AIBN} mol.1^{-1}	$c_{heptane}$ mol.1^{-1}
M	9.36	0.094	0.28	-
MH	6.94	0.069	0.17	1.64

with the styrene-divinylbenzene gel "Styragel" (Waters)
of different pore sizes, so that the system of columns
gave a linear calibration dependence in the required
molecular weight range. The flow of tetrahydrofuran
(THF) was 0.35 cm^3min^{-1}, c. 1.64 cm^3 of the polymer
solution was injected at concentrations of approx.
0.25% w/v. The universal calibration dependence (1) was
constructed by using linear polystyrene standards
(Waters) for which $[\eta] = 1.17\times10^{-2}M^{0.717}$ (14). From the
experimental elution curves of all samples, the ap-
parent average molecular weights were calculated using
universal calibration and the Mark-Houwink equation
$[\eta] = 1.08\times10^{-2}M^{0.702}$ valid for linear PMMA in THF at
25°C (14). Under the chosen experimental conditions of
separation, the disturbing dispersion was almost sup-
pressed, and chromatograms were therefore left uncor-
rected for longitudinal spreading.

Solution viscosities were measured in an Ubbelohde
dilution capillary viscometer in THF at 25°C. The in-
trinsic viscosity was extrapolated using Heller's
method.

Light scattering measurements were performed with
a FICA photogoniodiffusometer in unpolarized light,
wavelength 546.1 nm, angular range 30-150°C. The sol-
utions were purified in a Beckman L8-55 ultracentrifuge
(rotor SW.1, 15 000 r.p.m., 1 h). M_w was obtained by the
evaluation of experimental data using the Zimm method.

Osmometric measurements were carried out in
toluene at 30°C with an automatic membrane osmometer
Hallikainen. The M_n values were calculated from the
reduced pressure extrapolated to zero concentration.

RESULTS AND DISCUSSION

The SEC method was used in the investigation of
the hydrodynamic behaviour of randomly branched PMMA

prepared in a thermodynamically good medium (in bulk -
series M) and in Θ-conditions (in a mixture of the
monomer with 24 vol.% n-heptane - series MH) as shown
in Table 1. Characteristics obtained by recalculating
SEC data in the traditional manner (by using universal
calibration with linear standards) along with the
results of scattering and osmometric measurements are
summarized in Table 2.

In a detailed study of the hydrodynamic behaviour
of the PMMA samples (13) we observed a rise in visco-
sity depression (decrease of g' values) with increasing
"solvent power" which was particularly pronounced with
polymers having a higher degree of branching. This
phenomenon restricts the validity of the Zimm-Kilb
approximation (10) (cf. Eq. (1)) to the surroundings of
the Θ-temperature only. As this findings is at variance
with the assumptions on which the predicted elution in
SEC in good solvents is based (7), in our case
a greater deformation of the real differential distri-
bution curve occurs (Fig.1); in other words, the ap-
parent molecular weight distribution is narrower than
the proposed one (Fig.2). Whether, and if, this defor-
mation affects the $M_{n,app}$ value, cannot be decided,
because deviations from M_n, although in some cases
exceeding the limits given by the accuracy of osmometry
(Table 2), are nevertheless not systematic. For further
manipulation with the obtained SEC data we shall use
Shultz's finding that $M_{n,app} \cong M_n$. The suggested cor-
rection of $M_{w,app}$ does not however give the real M_w
obtained independently from scattering data, but a much
lower value, namely, by 10-30% (Fig.3). This trend is
the more pronounced, the more favourable conditions for
the formation of macrorings arise in the polymerization
(cf. series MH).

TABLE 2

Molecular Parameters of Random Branched PMMA Calculated from Measurements by Different Methods

Sample	Light scattering $M_w \times 10^{-5}$	Osmometry $M_n \times 10^{-5}$	Viscometry [η] [cm³ g⁻¹]	m_w	SEC data $M_{w,app} \times 10^{-5}$	$M_{n,app} \times 10^{-5}$
M 1	6.10	2.06	87	0.7	5.30	2.25
M 2	8.00	2.10	93	1.2	6.40	1.94
M 3	15.40	2.26	100	3.2	10.50	2.20
M 4	23.00	2.18	110	5.7	14.80	2.14
M 5*	11.80	–	147	–	10.30	3.29
M 6*	20.00	–	167	–	15.70	5.42
MH 1	4.70	1.40	56	0.9	3.40	1.36
MH 2	7.50	2.03	70	1.1	5.60	1.90
MH 3	15.50	2.10	78	3.6	0.00	2.40
MH 4	25.20	2.05	80	6.9	13.00	2.05

*Samples were prepared with lower AIBN concentration

$$\frac{dw}{d \log M}$$
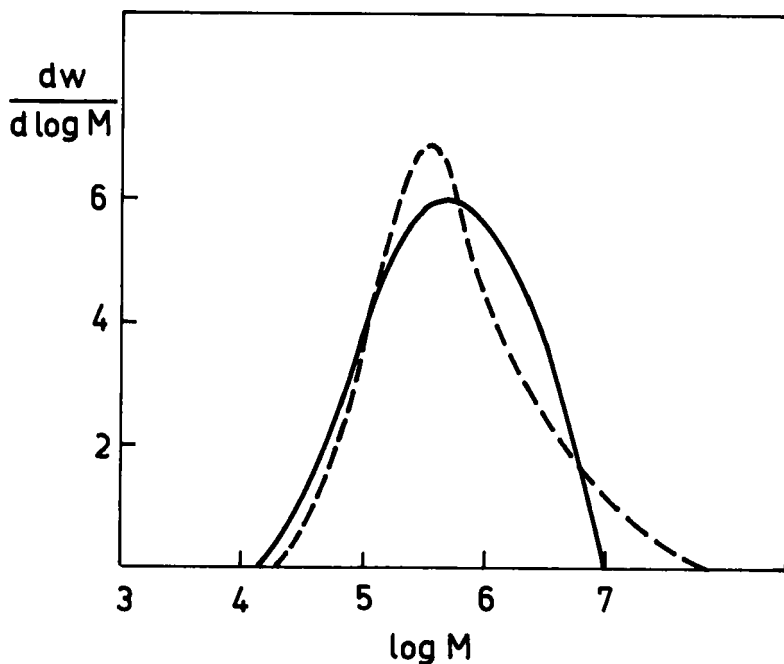
FIGURE 1   Differential distribution curve of sample M4
           ——— apparent, ----- real (calculated after
           Kilb (3)).

To obtain the real value of M_w, we must supplement
the SEC data with the experimentally determined [η] in
the eluent (THF). This value then appears in the fol-
lowing recalculation of $M_{w,app}$ to $M_{w,real}$ suggested
by us. For a molecularly monodisperse statistically
branched polymer we have (7)

$$M_{real,i} = g'^{(-\frac{1}{a+1})} M_{app,i} \qquad (2)$$

When g' is replaced with $[η]_{b,i}/[η]_{l,i}$ and $[η]_{l,i}$ is
replaced with $K(M_{real,i})^a$, Eq. (2) becomes
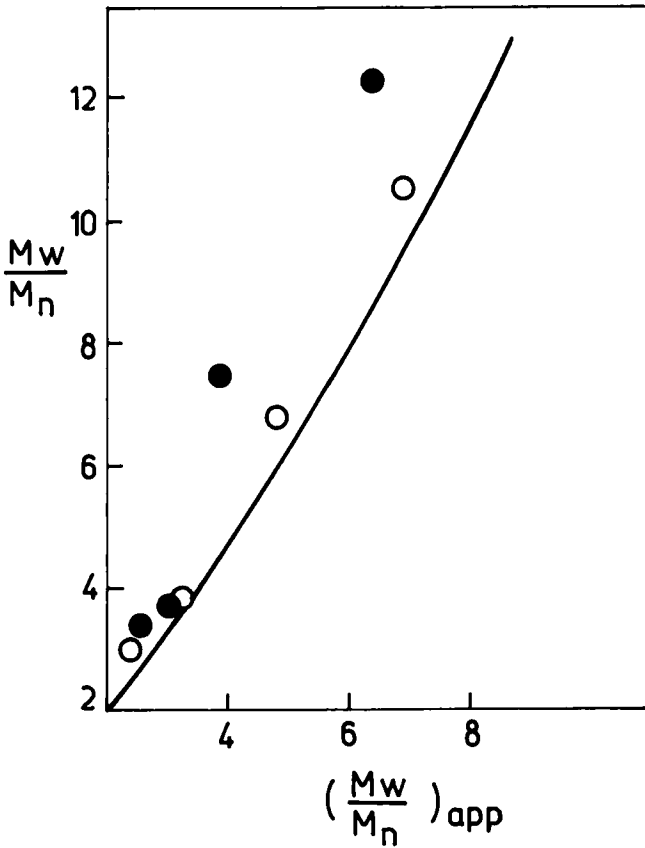
FIGURE 2   Dependence of the apparent width of molecular
           weight distribution on the real one (M_w/M_n)
           —— predicted by Shultz (7); O series M,
           ● series MH.

$$M_{real,i} = \frac{K}{[\eta]_{b,i}} (M_{app,i})^{a+1} \qquad (3)$$

After the necessary summation over all normalized
heights of the increments of the chromatographic curve
we obtain
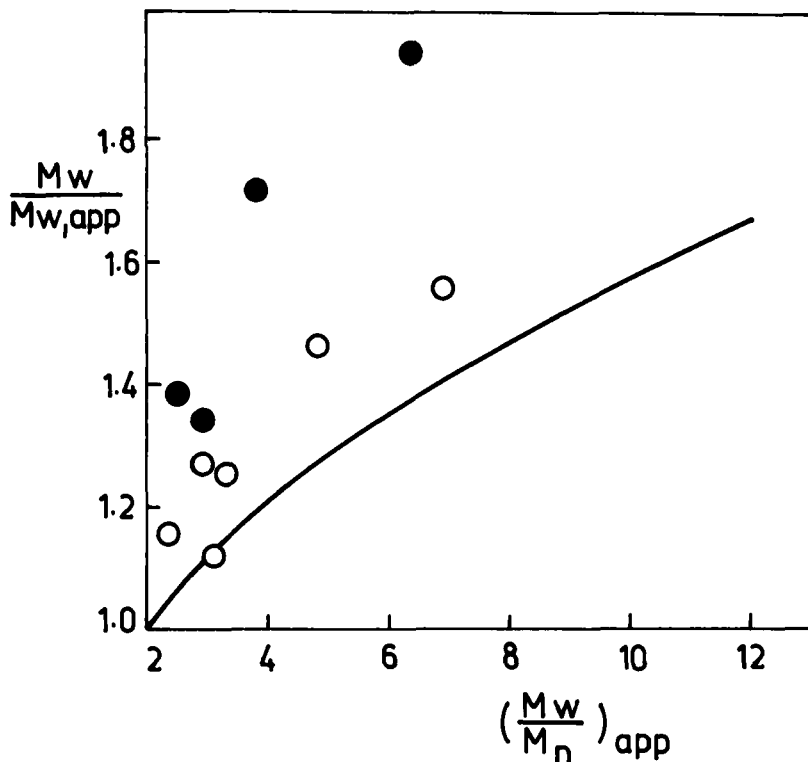
FIGURE 3   Correction of $M_{w,app}$ as a function of
$M_w/M_{n,app}$: O series M, ● series MH,
———— suggested by Shultz (7).

$$M_{w,real} = \frac{KQ}{[\eta]_b} (M_{w,app})^{a+1} \qquad (4)$$

The correction factor Q represents a decrease in in-
trinsic viscosity of the corresponding linear polymer
caused by polydispersity (i.e., of a polymer having the
same M_w, the same width (r = M_w/M_n) and type of mole-
cular weight distribution as the analyzed branched
polymer). The correction factors Q as a function of r

TABLE 3

Values of the Correction Factor Q

r	a			
	0.5	0.6	0.7	0.75
2.000	0.940	0.944	0.950	0.956
2.167	0.930	0.926	0.935	0.946
2.375	0.916	0.913	0.925	0.937
2.659	0.901	0.899	0.915	0.926
3.000	0.883	0.882	0.900	0.918
3.500	0.861	0.858	0.870	0.894
4.250	0.832	0.835	0.855	0.872
5.500	0.795	0.796	0.816	0.842
8.000	0.735	0.743	0.775	0.797
15.500	0.639	0.647	0.715	0.733
30.500	0.541	0.552	0.620	0.635

and of the exponent of the Mark-Houwink equation $\underline{a}$ are given in Table 3 (15). Conversion of $M_{w,app}$ to $M_{w,real}$ is carried out in the following way: First, in Eq. (4) Q is substituted for r_{app} while bearing in mind that the $M^*_{w,real}$ and r^* thus obtained are higher, but much closer to real values than the apparent values. The definitive $M_{w,real}$ value is calculated by using the Q factor corresponding to r^*, the error being $\Delta Q \leq 3\%$.

The $M_{w,real}$ and $M_{n,real}$ values obtained by the "off line" method lie predominantly in the range of the generally accepted experimental error of absolute methods as found independently by the light scattering and osmometric methods (Tables 2 and 4). The width of the real molecular weight distribution ($r = M_{w,real}/M_{n,real}$) may be used in the presented system as a measure of intermolecular branching. For instance, the weight average of intermolecularly bound tetra-

TABLE 4

Characteristics Obtained from SEC Data by Using the Proposed Correction

Sample	$M_{w,real} \times 10^{-5}$	Deviations from determinations by absolute methods				
		ΔM_w %	ΔM_w^* %	ΔM_n %	m_w	Υ
M 1	6.2	1.6	-9.6	9.2	0.5	0.33
2	7.6	-5.0	-8.8	-7.6	1.3	0.56
3	15.0	-2.6	-13.4	-2.6	3.2	0.76
4	23.1	0.4	-9.3	-1.8	5.9	0.85
5	11.1	-5.9	-1.4	-	0.9	0.48
6	19.5	-2.5	-13.6	-	1.1	0.50
MH 1	4.4	-6.4	-23.3	-2.8	0.8	0.45
2	7.9	5.3	-17.1	-6.4	1.4	0.59
3	14.9	-3.9	-30.9	14.3	2.8	0.74
4	25.0	-0.8	-28.8	0.0	7.0	0.87

*by using the correction predicted by Shultz (7)

functional branch units in the macromolecules is given by (3)

$$m_w = \frac{2(r-2)}{3} \qquad (5)$$

With respect to the extent of network formation, the branching index γ (10)

$$\gamma = \frac{2(r-2)}{2r-1} \qquad (6)$$

is often used in the pregel state. Its value varies in the range from 0 for an unbranched primary polydisperse polymer to unity, when gelation sets in. Both these parameters are given in Table 4.

The analysis of existing experimental findings on the chain (co)polymerization of bisunsaturated mono-mers generally admits the formation of macrorings (16). For this reason, the characterization of systems with randomly situated tetrafunctional branch units reported here may have a more general meaning and may be employed on a wider scale.

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