

## Molecular Weights of Styrene-Maleic Anhydride Copolymers\*

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### Synopsis

A dual-calibration method for the determination of molecular weights and molecular weight distribution of styrene-maleic anhydride copolymers (S/MA) by gel permeation chromatography (GPC) is introduced. It might be applicable to copolymers of other type. A linear relationship of intrinsic viscosity  $[\eta]$  and weight-average molecular weight ( $\bar{M}_w$ ) for unfractionated S/MA in tetrahydrofuran (THF) at 25°C can be expressed by the equation

$$[\eta] = 3.98 \times 10^{-4} \bar{M}_w^{0.596}$$

The maleic anhydride content of the copolymers ranges from 5 to 50 mole-%, and the  $\bar{M}_w$  range is from  $2 \times 10^4$  to  $7 \times 10^6$ . The plot of  $\log [\eta] \bar{M}_w$  versus GPC elution volume of the S/MA copolymers falls on the same curve as that of the polystyrene standards in THF.

### INTRODUCTION

Since its introduction by Moore<sup>1</sup> in 1964, gel permeation chromatography (GPC) has become the most powerful tool for the rapid determination of molecular weight (MW) and molecular weight distribution (MWD) of polymers. However, it has been limited to a small number of homopolymers due to the lack of well-characterized standards. The extension of the idea to the study of copolymers is even rare due to the more complicated systems.

The Mark-Houwink's expression  $[\eta] = KM^a$  has held best for fractionated, linear homopolymers. Although this relationship of intrinsic viscosity with MW has been obtained for a few copolymers,<sup>2,3</sup> the composition of most copolymers studied had the same average composition in the series since the azeotropic copolymers were used.

Few applications of it to copolymers of varying composition have been reported in literature. This is principally due to the general belief that copolymers varying in chain composition would have no consistent relationship between  $[\eta]$  and their MW.

This paper proposes the determination of MW and MWD of styrene-maleic anhydride (S/MA) copolymers by a GPC dual-calibration method which might be also applicable to copolymers of other type, and shows how the  $[\eta] = KM^a$  equation applies successfully to S/MA copolymers of broad composition and MW ranges.

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TABLE I  
 Molecular Weights and Composition of S/MA<sup>a</sup>

Sample no	A	B	C	D	E	F
	$\bar{M}_n$ by osmometer	$\bar{M}_w$ by light scattering	GPC $\bar{M}_n$ after adjustment	GPC $\bar{M}_w$ based on adjusted $\bar{M}_n$ calibration	GPC $\bar{M}_w$ after adjustment	MA, mole-%
6	82,000	134,000	82,000	175,000	134,000	4.7
12	158,000	278,000	147,000	345,000	265,000	5.0
14	174,000	351,000	188,000	457,000	350,000	5.1
15	180,000	360,000	177,000	431,000	340,000	17.7
7	117,000	186,000	121,000	288,000	221,000	18.1
5	75,000	132,000	84,000	184,000	141,000	18.0
9	108,000	241,000	112,000	288,000	220,000	24.7
10	145,000	253,000	136,000	251,000	269,000	24.9
3	80,000	112,000	79,000	178,000	136,000	25.4
8	95,000	200,000	94,000	227,000	180,000	32.7
34	75,000	135,000	65,000	146,000	112,000	32.9
11	126,000	271,000	92,000	281,000	216,000	32.9
35		349,000		438,000	333,000	
36	156,000		159,000			50
37	159,000		153,000			50
38	165,000		162,000			50
39	172,000		175,000			50
40	174,000		177,000			50

<sup>a</sup> Calibration curve for polystyrene:  $\text{count} = 77.7 - 7.5 \log \bar{M}$ ; calibration curve for S/MA ( $\bar{M}_n$ ):  $\text{count} = 77.85 - 7.35 \log \bar{M}$ ; calibration curve for S/MA ( $\bar{M}_w$ ):  $\text{count} = 77.0 - 7.35 \log \bar{M}$ .

A universal calibration curve for all polymer types by plotting  $\log [\eta] \bar{M}_w$  against elution volume has been suggested.<sup>4</sup> It is also investigated using the S/MA copolymers in this paper.

## EXPERIMENTAL

### Materials

All copolymer samples were supplied by Evani, Kent, and Wayt of Dow Chemical U.S.A. They were prepared either in methyl ethyl ketone or methylene chloride solution. The maleic anhydride content of the samples varied from 5 to 50 mole-%.

### Gel Permeation Chromatography (GPC)

The study was conducted with a Waters Associates unit Model 100 in tetrahydrofuran (THF). A flow rate of 1 ml/min was used. A series of seven columns designated by Waters Associates as of  $10^6$ ,  $10^5$ ,  $5 \times 10^4$ ,  $3 \times 10^4$ ,  $2 \times 10^4$ ,  $2 \times 10^4$ ,  $10^3$  Å was used. The sample solution (0.25% by weight in THF) was injected for a period of 2 min after being filtered with a Millipore pressure filter using a 35-mm Krueger filter pad. A theoretical plate count of the column combination was 740 plates/ft for trichlorobenzene.

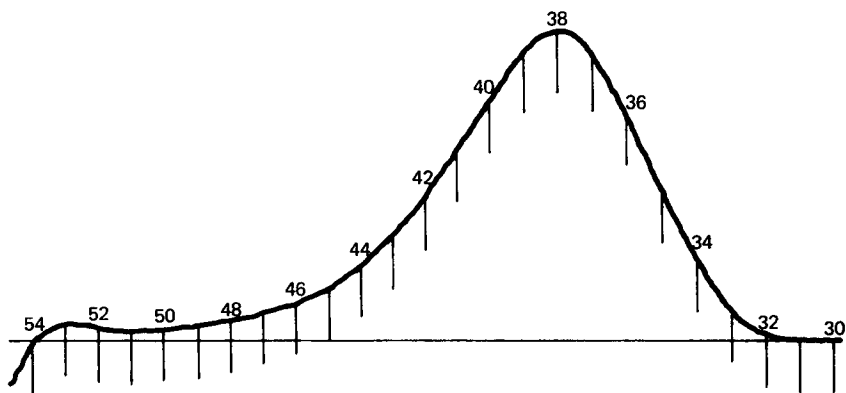


Fig. 1. Chromatogram of sample 11.

### Dual GPC Calibration Method

The weight-average molecular weight ( $\bar{M}_w$ ) and number-average molecular weight ( $\bar{M}_n$ ) of the copolymers were determined by light-scattering photometry and membrane osmometry, respectively. They were also calculated from the GPC chromatogram using a linear polystyrene calibration curve without spreading correction as a first approximation. Two calibration curves, one for each average molecular weight ( $\bar{M}$ ), can be established by trial and error of the intercept and slope of the calibration line with the help of a computer until each of the GPC- $\bar{M}$  matches the respective "absolute" values. The two calibration curves can then be used for each  $\bar{M}$  determination.

### Intrinsic Viscosity

Intrinsic viscosities of copolymers were determined in THF (Burdick & Jackson Lab., Inc.) at 25°C in Ostwald-Fenske viscometer. Flow time for the solvent was in excess of 100 sec.

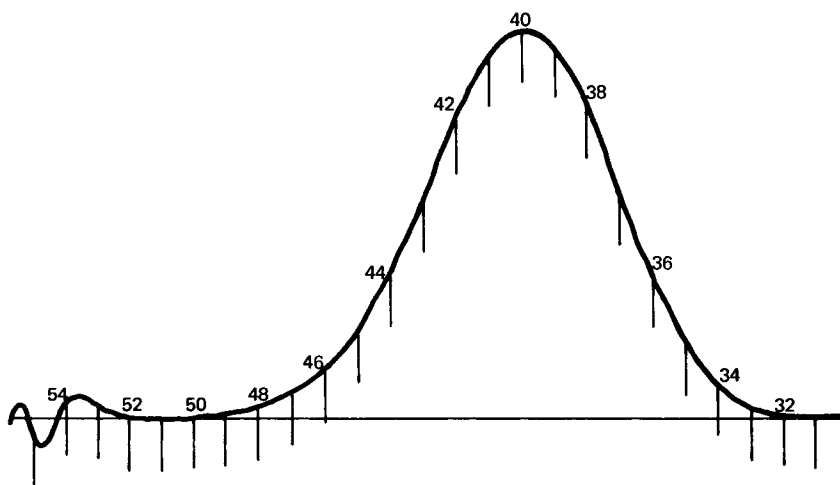


Fig. 2. Chromatogram of sample 9.

## Light-Scattering Photometry

The weight-average molecular weights ( $\bar{M}_w$ ) of the samples were determined by light-scattering measurement. The sample solutions in THF were rendered free from dust by pressure filtering as described in the GPC section and by centrifuging for 2 hr at 15,000 rpm. The measurements were made

TABLE II  
Relationship of Intrinsic Viscosity and Molecular Weight of S/MA<sup>a</sup>

Sample no.	Light-scattering molecular weight	Viscosity		Per cent difference	MA, mole-%
		Observed	Calculated		
1	22,500	0.100	0.156	35.911	50
2	87,200	0.290	0.350	17.102	50
3	112,000	0.450	0.406	-10.809	25.4
4	124,200	0.360	0.432	16.651	50
5	132,200	0.470	0.448	-4.843	18
6	134,000	0.490	0.452	-8.427	4.7
7	186,000	0.750	0.549	-36.499	18.1
8	200,000	0.610	0.574	-6.320	32.7
9	240,900	0.710	0.641	-10.760	25
10	253,000	0.810	0.660	-22.723	24.9
11	271,000	0.760	0.688	-10.526	33
12	278,400	0.780	0.699	-11.628	4.7
13	316,000	0.710	0.754	5.779	50
14	351,000	0.960	0.802	-19.666	5.1
15	360,000	0.880	0.814	-8.051	17.7
16	446,000	0.940	0.925	-1.585	50
17	476,800	0.790	0.963	17.957	50
18	513,000	1.040	1.006	-3.397	50
19	858,000	1.440	1.367	-5.369	50
20	1,050,000	1.910	1.541	-23.912	50
21	1,071,000	1.620	1.560	-3.865	50
22	1,445,000	1.850	1.865	0.779	50
23	1,591,000	1.910	1.975	3.273	50
24	1,812,700	1.485	2.134	30.421	50
25	2,352,700	1.825	2.493	26.798	50
26	2,786,000	3.180	2.757	-15.328	50
27	3,473,000	3.600	3.144	-14.488	50
28	3,777,000	3.040	3.306	8.087	50
29	3,975,200	3.950	3.408	-15.903	50
30	4,398,000	3.190	3.620	11.869	50
31	5,293,500	5.060	4.042	-25.175	50
32	6,624,000	4.030	4.620	12.776	50
33	6,869,000	3.690	4.721	21.845	50

<sup>a</sup> Viscosity =  $3.9753 \times 10^{-4} \times M^{0.996}$  Coefficient of correlation = 0.980; coefficient of determination = 0.959.

with a light-scattering photometer (Mechrolab Model 701) at room temperature. Mercury line (5460 Å) was used as the source of light and pure benzene as calibration standard. Intensities of scattered light were measured in each case at a series of angles from 30° to 105° for five concentrations of the sample in THF. Refractive index increment of samples was determined with a differential refractometer (Phoenix Precision Instrument Co.).

TABLE III  
Calculation of  $[\eta] \bar{M}_w$  for Polystyrene Standards and S/MA Copolymers

	$\bar{M}_w$	$[\eta]^a$	$[\eta] \bar{M}_w$	Elution counts (5 ml/count)
Polystyrene standards				
	830,000	2.4155	2,005,000	33.3
	402,000	1.4477	582,000	35.7
	171,000	0.7905	135,000	38.4
	97,200	0.5308	51,600	40.3
	50,000	0.3319	16,600	42.5
	19,750	0.1726	3,400	45.5
	10,000	0.1067	1,070	47.7
	4,800	0.0759	390	50.1
S/MA Copolymer no.				
5	132,000	0.47	62,100	40.0
6	134,000	0.49	65,700	40.2
8	200,000	0.61	122,000	38.9
9	241,000	0.71	171,000	38.2
11	271,000	0.76	206,000	38.0
12	278,000	0.78	217,000	37.9
10	253,000	0.81	205,000	37.5
15	360,000	0.88	317,000	36.8
14	351,000	0.96	337,000	36.7

<sup>a</sup>The  $[\eta]$  of polystyrene standards were calculated using the  ${}^9[\eta]_{25}^{\text{THF}} = 1.60 \times 10^{-4} \times \bar{M}_w^{0.706}$ .

### Membrane Osmometry

The number-average molecular weight ( $\bar{M}_n$ ) measurements were made with a recording osmometer Model CSM-2 (Melabs) in THF. The osmotic pressures of solutions of four concentrations were measured. The  $\bar{M}_n$  was calculated from the osmotic pressure/concentration ratio with concentration extrapolating to zero.

### RESULTS AND DISCUSSION

The samples used in this study were made with a continuous polymerization process<sup>5</sup> which resulted in narrow composition distribution. The maleic anhydride (MA) content of most of the samples have a fluctuation of less than 3% across the total molecular weight ranges. Their relatively narrow molecular weight distributions can be expressed by the ratios of  $\bar{M}_w$  and  $\bar{M}_n$  which are close to 2.

The  $\bar{M}_n$  and  $\bar{M}_w$  of the samples determined by osmometry and light-scattering measurements are listed in columns A and B of Table I, respectively. The table shows that the  $\bar{M}_n$  obtained by the dual GPC calibration (column C) match very well with those of osmometry values for MA content up to 50 mole-%. Two out of three values for MA of 33 mole-% (samples 8, 34, and 11) were not in good agreement. It is known that the  $\bar{M}_n$  is very sensitive to the presence of low molecular weight (LMW) species which happened to be present in both of the samples (Fig. 1). The LMW "trail" was either absent

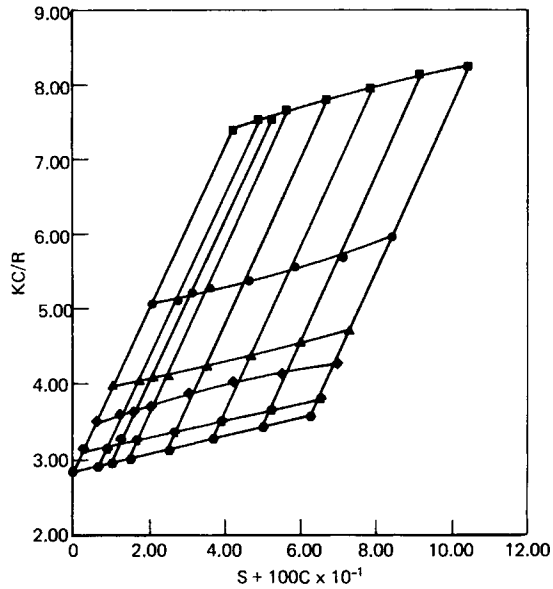


Fig. 3. Typical Zimm plot S/MA.

or not so prominent in the rest of the samples (Fig. 2). It is believed at this stage that this discrepancy between GPC and osmometry  $\bar{M}_n$  in those two samples was due to the existence of LMW "tail."

The GPC  $\bar{M}_w$  calculated from the adjusted  $\bar{M}_n$  calibration curve (column D of Table I) were much too high as compared with the light-scattering data. This is because the  $\bar{M}_n$  calibration was based on  $\bar{M}_n$  of broad MWD samples instead of narrow MWD standards. The osmometry  $\bar{M}_n$  values are usually higher than the actual  $\bar{M}_n$  due to the escape of small molecules through the

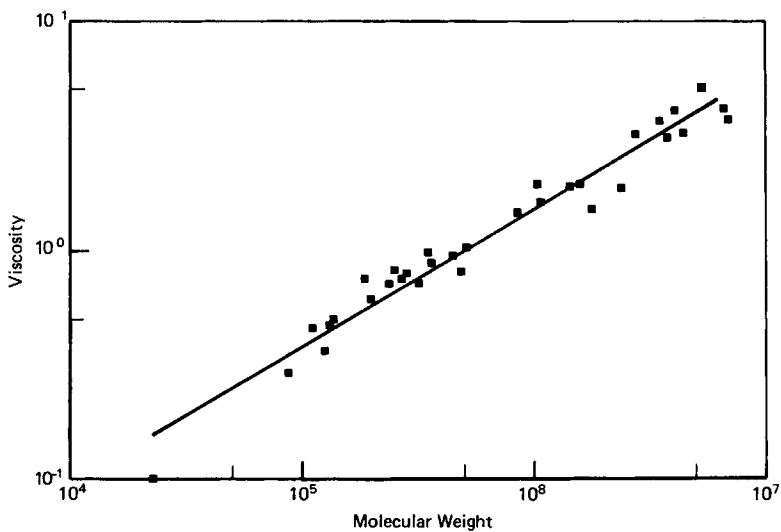


Fig. 4. Relationship of intrinsic viscosity and molecular weight of S/MA.

membrane, while the GPC  $\bar{M}_w$  are usually higher than the light-scattering  $\bar{M}_w$  due to the broadening effect. Therefore, the adjustment of the calibration curve according to osmometry  $\bar{M}_n$  would certainly result in a much higher GPC  $\bar{M}_w$  than the actual  $\bar{M}_w$ . The GPC values were adjusted according to the dual GPC calibration method and the adjusted  $\bar{M}_w$  (column E of Table I) were in excellent agreement with the light-scattering values (column B of Table I).

It has been known that the light-scattering treatment generally applicable to the analysis of polymers for the determination of  $\bar{M}_w$  yields only an apparent value ( $M_{ap}$ ) in the case of copolymer. The real molecular weight can be

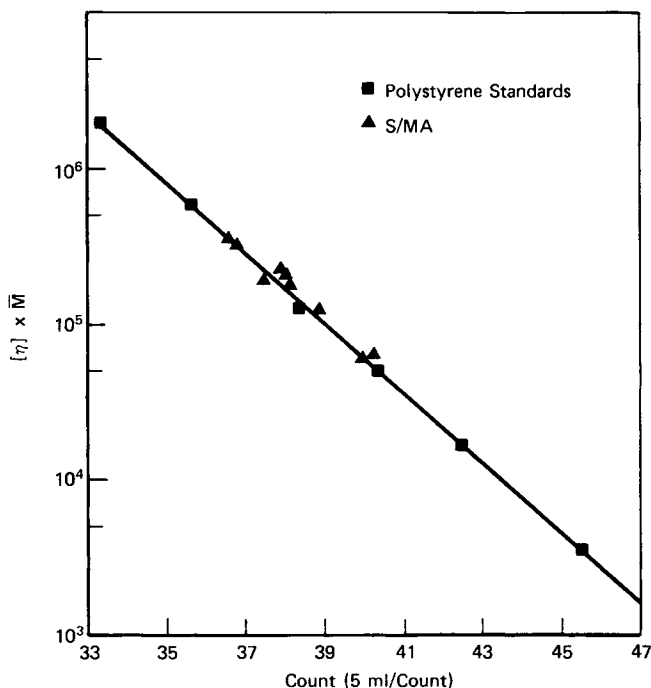


Fig. 5. Calibration curve for polystyrene and S/MA copolymers.

obtained by running three sets of measurements in different solvents based on the well tested equation of Bushuk and Benoit<sup>6,7</sup> for binary copolymers:

$$M_{ap} = M_w + 2P[(V_A - V_B)/V_0] + Q[(V_A - V_B)/V_0]^2$$

in which  $M_w$  is the true  $\bar{M}_w$ ,  $V_A$  and  $V_B$  are the refractive index increments of homopolymers A and B, respectively, and  $V_0$  is the measured refractive index increment of the copolymer-solvent system,  $P$ ,  $Q$  are related to the polydispersity of chain composition. However, the refractive index increments of the S/MA-THF system were very high, and the apparent MW were probably as close as the true  $\bar{M}_w$ .

Some data of light-scattering measurements and intrinsic viscosities are shown in Table II. A typical Zimm plot<sup>8</sup> is demonstrated in Figure 3. The light-scattering  $\bar{M}_w$  and  $[\eta]$  relationship in Table II was treated with the

least-square method and is plotted as in Figure 4. The curve can be expressed by the following equation:

$$[\eta] = 3.98 \times 10^{-4} \bar{M}_w^{0.596}.$$

The  $\log [\eta] \bar{M}_w$  against elution volume plot gave a single-calibration curve in GPC for many polymers of various shapes. The  $[\eta] \bar{M}_w$  calculations were made in Table III for S/MA copolymers and polystyrene standards. The two polymers fit the same curve as shown in Figure 5. This certainly supports the hypothesis that the viscometric hydrodynamic volume, characterized by  $[\eta] \bar{M}_w$ , might be the controlling factor in determining separation in GPC.

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