

# Determination of the Absolute Molecular Weight of a Styrene-Butyl Acrylate Emulsion Copolymer by Low-Angle Laser Light Scattering (LALLS) and GPC/LALLS

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## Synopsis

The application of low-angle laser light scattering (LALLS) and combined GPC/LALLS for the measurement of absolute molecular weight distribution of a styrene-butylacrylate (30/70) emulsion copolymer is discussed. From the static light scattering measurements in four different solvents, i.e., toluene, tetrahydrofuran (THF), methyl ethyl ketone (MEK), and dimethylformamide (DMF), the true weight average molecular weight ( $\bar{M}_w$ ) and heterogeneity parameters are determined. The apparent  $\bar{M}_w$  obtained from the static measurement in THF was in good agreement with the  $\bar{M}_w$  determined from the multiple solvent analysis, suggesting the validity of using THF as the mobile phase in the combined GPC/LALLS analysis.

## INTRODUCTION

The interpretation of light scattering data for copolymer systems is particularly difficult due to the heterogeneity of chemical composition. The correct treatment of light scattering measurements for copolymers in general requires measurements in at least three solvents of different specific refractive index increments. The theory and general equations developed by Bushuk and Benoit<sup>1</sup> and Stockmayer<sup>2</sup> provide the true weight average molecular weight of the copolymer along with parameters which characterize the heterogeneity of the chemical composition in the system.

The development of the theory has been described in detail elsewhere and has been treated in reviews.<sup>1-5</sup> Therefore, only mathematical expressions pertinent to the present work will be discussed briefly.

Based on the assumption of linearity between the specific refractive index increment and the weight fraction of copolymer composition, an expression has been derived yielding the true weight-average molecular weight  $\bar{M}_w$  and the heterogeneity parameters  $P$  and  $Q$ .<sup>1,2</sup> For a copolymer system comprised of two kinds of repeating units, A and B, with heterogeneity in both molecular weight and composition the expression takes the form

$$\bar{M}_w^* = \bar{M}_w + 2Pb + Qb^2 \quad (1)$$

$$b = (\nu_a - \nu_b)/\nu. \quad (2)$$

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In the above expressions,  $\bar{M}_v^*$  is the observed or apparent molecular weight,  $\bar{M}_w$  is the true molecular weight,  $\nu$  is the specific refractive index increment of the copolymer, and  $\nu_a$  and  $\nu_b$  are the specific refractive index increments of the homopolymers A and B, respectively. The parameters  $P$  and  $Q$  are weighted measures of the heterogeneity in composition of the copolymer. These parameters are properties of the copolymer and independent of the solvent used for the light scattering experiments.<sup>4</sup>

The purpose of this work is to illustrate the applicability of the above theory to the characterization of a styrene-butyl acrylate emulsion (30/70) copolymer using a low-angle laser light scattering photometer. The use of LALLS in conjunction with a GPC for the analysis of molecular weight distribution also is discussed.

## EXPERIMENTAL

**Synthesis.** The styrene-butyl acrylate copolymer was prepared by emulsion polymerization using anionic surfactant and potassium persulfate as initiator. The monomer composition of styrene and butyl acrylate was 30% styrene and 70% butyl acrylate, respectively. The copolymerization was performed at 75°C with monomer fed over a period of 3 h. Conversion for this system was 96%.

**Sample Preparation.** Gel free samples were dried at 70°C and then vacuum-dried. Dry copolymer samples were dissolved in the appropriate solvents by mechanical shaking at room temperature. The solutions were filtered through a 0.45- $\mu$  teflon filter (Millipore) and four concentrations in the range of 2–8 mg/mL were prepared for light scattering measurements. The solvents used were toluene, dimethyl formamide (DMF), methyl ethyl ketone (MEK), and tetrahydrofuran (THF).

**Low-Angle Laser Light Scattering (LALLS).** The specific refractive index increments were measured at  $\lambda = 633$  nm wavelength at 20°C, with a Chromatix KMX-16 differential refractometer (Chromatix, Inc., Sunnyvale, Calif.).

The light scattering measurements were performed by a Chromatix KMX-6, LALLS Photometer. The measurements conditions were 633 nm wavelength, 20°C, and 6–7° angle. Details of the instrumentation and operation of KMX-6 and KMX-16 are described elsewhere.<sup>6–8</sup> The use of LALLS for light scattering measurements significantly reduces the time involved in the analysis of light scattering data, by eliminating the need for angular extrapolation in conventional total intensity light scattering. However, when working with this instrument, particular care must be taken with respect to proper optical alignment, filtration of the sample, and removal of bubbles in the sample cell in order to obtain accurate results. Furthermore, experience indicates that small amounts of high molecular weight polymer, due to the presence of microgel in the sample or aggregation can result in unexpected large values for  $\bar{M}_w$ , which can lead to errors in interpretation about the nature of the sample.

**GPC/LALLS Analysis.** For GPC/LALLS analyses the LALLS photometer was connected to a 150C ALC/GPC (Water Associates, Milford, Mass.). Both the high performance gel permeation chromatograph (HPGPC) and the LALLS detector were interfaced with a MINC microcomputer (Digital Equipment Corp., Maynard, Mass.) for data acquisition and data analysis.

The HPGPC included a  $\mu$ Styragel column set consisting of 100, 500, 10<sup>3</sup>, 10<sup>4</sup>,

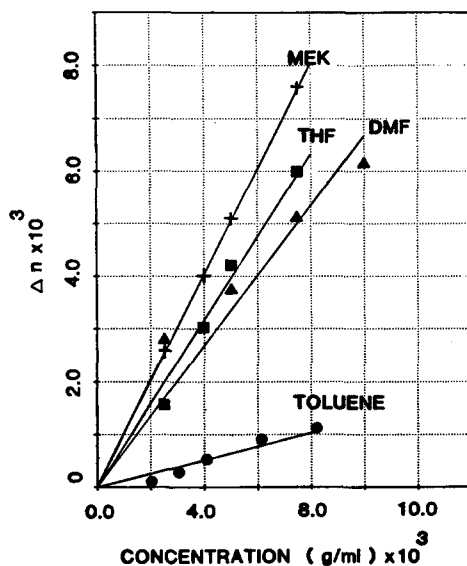


Fig. 1. Refractive index increment vs. concentration plots for the S/BA copolymer in four different solvents: (●) toluene; (▲) DMF; (■) THF; (+) MEK.

$10^5$ , and  $10^6$  Å columns. ( $\mu$ Styragel is a Registered Trademark of Waters Associates, Milford, Mass.) For GPC/LALLS analysis a  $200 \mu\text{L}$  sample volume of 0.5% (w/v) concentration was injected onto the columns. The solvent flow rate was set at 1 mL/min. THF was used as the mobile phase. All experiments were performed at  $30^\circ\text{C}$ .

## RESULTS AND DISCUSSION

**Measurement of Specific Refractive Index Increment ( $dn/dc$ ).** Figure 1 shows the data for the measurement of the specific refractive index increment. For each solvent the change in the specific refractive index increment of the solution with respect to concentration is shown. Solid lines indicate the best fit for each set of data obtained from linear regression analysis. The slope of each line is a measure of the specific refractive index increment in the corresponding solvent. Results are summarized in Table I.

In a separate experiment it was shown that the  $dn/dc$  value of the copolymer in each solvent is a linear superposition of the sum of the product of the weight fraction times the  $dn/dc$  value for each homopolymer component.

TABLE I  
Summary of Static LALLS Experiments

	$n$	$\nu_S$	$\nu_{BA}$	$\nu_{S/BA}$	$\bar{M}_w^* \times 10^{-5}$ (g/mol)	$A \times 10^4$	$b$
Toluene	1.49	0.111	-0.024	$0.021 \pm 0.002$	$3.10 \pm 0.36$	2.06	6.43
DMF	1.43	0.165	0.016	$0.061 \pm 0.008$	$2.19 \pm 0.39$	2.03	2.44
THF	1.40	0.193	0.067	$0.112 \pm 0.007$	$1.39 \pm 0.31$	2.13	1.13
MEK	1.38	0.214	0.097	$0.137 \pm 0.001$	$1.58 \pm 0.28$	5.83	0.89

**Static LALLS Experiments.** The data from the static LALLS experiments ( $Kc/\bar{R}_\theta$ ) are shown in Figure 2. The reciprocal scattering function vs. the concentration of the polymer solution is shown for each solvent. The data analysis of the light scattering experiments for the limit of small angle ( $6-7^\circ$ ) is carried out according to the following equations<sup>6,7</sup>:

$$Kc/\bar{R}_\theta = 1/\bar{M}_w + 2A_2c \quad (3)$$

where  $\bar{M}_w$  is the weight average molecular weight,  $A_2$  is the second virial coefficient, and  $K$  is an optical constant defined as

$$K = \frac{2\pi^2 n^2}{\lambda_0^4 N} \left( \frac{dn}{dc} \right)^2 (1 + \cos^2 \theta). \quad (4)$$

$\bar{R}_\theta$  is the excess Rayleigh factor and is measured experimentally and  $c$  (g/mL) is the concentration of the polymer.  $\theta$  is the scattering angle,  $n$  is the refractive index of the solvent, and  $\lambda_0$  is the wavelength of the laser (633 nm). Linear regression analysis of  $Kc/\bar{R}_\theta$  vs.  $c$  for each set of data results in the corresponding apparent  $\bar{M}_w^*$  and  $A_2$  values for the respective polymer-solvent system. Results also are summarized in Table I. The values of the parameter  $b$  calculated for each solvent from eq. (2) also are shown in Table I.

A plot of the apparent molecular weight  $\bar{M}_w^*$  vs.  $b$  is shown in Figure 3. In order to determine the true molecular weight of the copolymer ( $\bar{M}_w$ ), one should find the best fit for  $\bar{M}_w^*$  vs.  $b$  to the parabolic function in eq. (1). An iterative search routine was used to find the best fit. Briefly, one can transform eq. (1) as follows:

$$Y_i = 2P + b_i Q \quad (5)$$

$$Y_i = ([\bar{M}_w^*]_i - \bar{M}_w)/b_i \quad (6)$$

where  $i$  refers to each solvent system. In this work, there is a total of four values

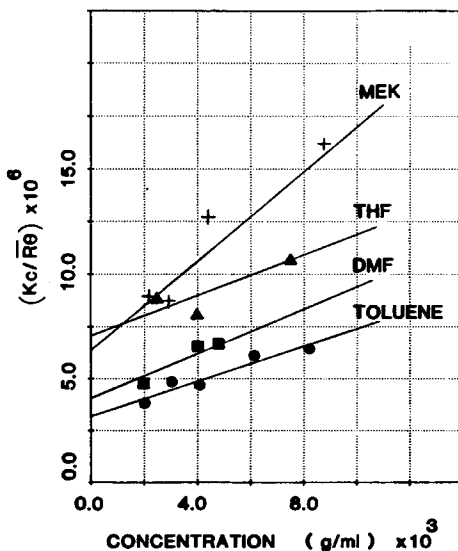


Fig. 2. Rayleigh ratio vs. concentration plots for the S/BA copolymer in four different solvents: (●) toluene; (■) DMF; (▲) THF; (+) MEK.

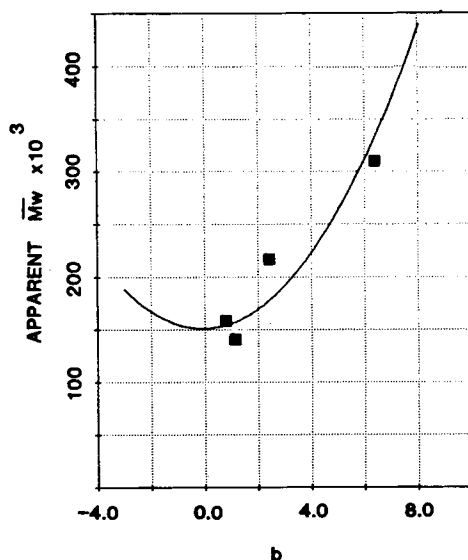


Fig. 3. Apparent molecular weight ( $\bar{M}_w^*$ ) vs. parameter  $b$ . The solid line indicates the best fit for data to the parabolic function in eq. (1).

of  $Y$  based on the four solvents used in the experiments. The following steps summarize the curve fitting procedure:

1. For an initial guess of  $\bar{M}_w$ , calculate  $Y_i$  from eq. (6) for values of  $\bar{M}_{wi}^*$  and  $b_i$  as given in Table I.

2. Perform a linear regression of  $Y$  vs.  $b_i$  [i.e., eq. (5)], based on the calculated values of  $Y_i$ , and determine  $P$ ,  $Q$ , and the correlation coefficient  $R$ .

3. Repeat steps 1 and 2 until the largest correlation coefficient is obtained for the linear regression within the theoretical limits of parameters  $P$  and  $Q$ .

The search method for the best fit to the experimental data results in

$$\bar{M}_w^* = 1.51 \times 10^5 + 5.73 \times 10^2 b + 4.37 \times 10^3 b^2 \quad (7)$$

Equation (7) describes a parabola which has a minimum at  $b = -0.07$  and  $\bar{M}_w^* = 1.51 \times 10^5$ . The molecular weight at the minimum corresponds to the actual weight average molecular weight of the copolymer. A plot of eq. (7) also is shown in Figure 3. According to eq. (1),

$$\bar{M}_w = 1.51 \times 10^5$$

$$P = 2.87 \times 10^2$$

$$Q = 4.37 \times 10^3$$

No attempt was made in this work to verify the values obtained for parameters  $P$  and  $Q$  by other means. The values for  $P$  and  $Q$  obtained here, however, appear to be considerably higher than what would be expected for a statistical copolymer from copolymerization theories (i.e.,  $P = 0$  and  $Q$  very small<sup>4</sup>). Similar results have been observed by others as reported in the literature,<sup>4,5</sup> which tend to indicate that the heterogeneity parameters for statistical copolymers as obtained from the light scattering experiment are usually unreliable.<sup>9</sup>

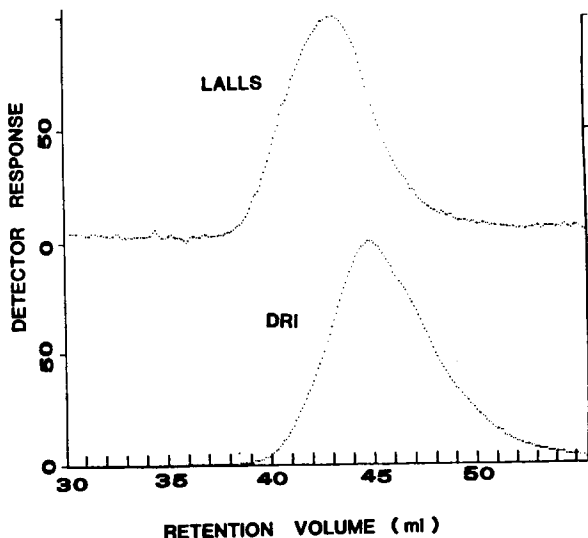


Fig. 4. DRI and LALLS chromatogram of the S/BA copolymer in THF.

The true value of the molecular weight  $\bar{M}_w$  in this case appears to be fairly close to the apparent  $\bar{M}_w^*$  as obtained for the copolymer in THF and MEK (i.e., solvents with highest  $dn/dc$ ). This conclusion suggests that in order to determine the actual molecular weight distribution for this copolymer one can use either THF or MEK as the mobile phase in the combined GPC/LALLS analysis with good accuracy. We have chosen THF in our analysis, and the results are discussed below.

**GPC/LALLS Analysis.** The raw chromatograms corresponding to the LALLS and DRI detector response for GPC/LALLS analysis of the copolymer is shown in Figure 4. The molecular weight statistics are calculated from the two chromatograms according to the data reduction technique described by Jordan<sup>8</sup> and are shown in Table II.

In analyzing the data from the GPC/LALLS experiment the second virial coefficient  $A_2$  for the whole polymer as obtained from the static LALLS measurements was used. This assumption, however, is probably not valid for individual species with heterogeneity in composition and molecular weight. One might expect the accuracy of results to be effected by this assumption.

Results of the GPC/LALLS analysis are shown in Table II. Corresponding results obtained for the same sample using conventional GPC (using DRI de-

TABLE II  
Average Molecular Weights Obtained for the Styrene/Butyl Acrylate (30/70) Emulsion Copolymer by LALLS and GPC/LALLS Analysis

	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$
GPC/LALLS	63.3	140
LALLS (multiple solvent)	—	151
GPC (calibration with polystyrene standards)	58.7	126

tor only) based on calibration with standard polystyrene samples also are shown in Table II.

The  $\bar{M}_w$  value by GPC/LALLS appears to be about 10% higher than the  $\bar{M}_w$  value obtained from the conventional GPC. This discrepancy is in part due to the fact that the composition of the copolymer sample is different from those used in column calibration. Another possible explanation of the higher  $\bar{M}_w$  values for GPC/LALLS analysis may be due to the larger sensitivity of the LALLS detector to the higher molecular weight fractions as compared with the concentration detector.

The  $\bar{M}_w$  obtained from GPC/LALLS analysis is 7% lower than that of static LALLS measurements using the multiple solvent technique. The agreement is good considering the fact that instrument spreading corrections were not made in the interpretation of GPC data.

### SUMMARY

In this work we have demonstrated the application of LALLS and GPC/LALLS in THF for molecular weight analysis of a binary copolymer. From the static LALLS experiments the true  $\bar{M}_w$  of a styrene/butyl acrylate (30/70) emulsion copolymer was obtained by fitting the apparent  $\bar{M}_w^*$  values determined in a series of solvents, to the model developed by Bushuk and Benoit and Stockmayer. In addition to the weight average molecular weight, the parameters which reflect the heterogeneity in composition of the copolymer also were obtained from the static measurements.

Results of static LALLS measurement using multiple solvent technique were in good agreement with the values obtained by operating the LALLS in conjunction with a high performance GPC using THF as mobile phase. The magnitude of the heterogeneity parameters  $P$  and  $Q$  obtained for this sample were considerably higher than what would be expected for a statistical copolymer from the copolymerization theory. This tends to agree with the conclusions reported by others<sup>4,5</sup> concerning difficulties in interpretation of such parameters as derived from the light scattering data in the case of the random copolymers.

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