very successful in that it predicts v_{2m} to be only slightly dependent on junction functionality and to have a value quite close to that obtained experimentally.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the National Science Foundation, through Grant No. DMR 77-18356 (Polymers Program, Division of Materials Research), and the postdoctoral fellowship awarded M.A.L. through the Joint Spain-United States Treaty for Scientific and Technological Cooperation. We also wish to acknowledge the very helpful advice, and other assistance, provided by Dr. J. R. Falender of the Dow Corning Corporation.

References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, New York, 1953.
(2) Treloar, L. R. G. "The Physics of Rubber Elasticity", 3rd ed.; Clarendon: Oxford, 1975.
(3) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, 351, 351.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(6) Duiser, J. A.; Staverman, A. J. In "Physics of Non-Crystalline Solids"; Prins, J. A., Ed.; North Holland: Amsterdam, 1965.
(7) Graessley, W. W. *Macromolecules* **1975**, *8*, 186, 865.
(8) Mark, J. E.; Sullivan J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(9) Sullivan, J. L.; Mark, J. E.; Hampton, P. G., Jr.; Cohen, R. E. *J. Chem. Phys.* **1978**, *68*, 2010.
(10) Mark, J. E.; Rahalkar, R. R.; Sullivan, J. L. *J. Chem. Phys.* **1979**, *70*, 1794.
(11) Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1979**, *71*, 682.
(12) Mark, J. E. *Makromol. Chem., Suppl. 2* **1979**, *180*, 87.
(13) Mark, J. E.; Llorente, M. A. *J. Am. Chem. Soc.*, **1980**, *102*, 632.
(14) Llorente, M. A.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 181.
(15) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *72*, 2282.
(16) Valles, E. M.; Macosko, C. W. *Rubber Chem. Technol.* **1976**, *49*, 1232.
(17) Valles, E. M.; Macosko, C. W. In "Chemistry and Properties of Cross-Linked Polymers"; Labana, S. S., Ed.; Academic Press: New York, 1977.
(18) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 673.
(19) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Chem. Phys.* **1979**, *70*, 5324.
(20) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7353.
(21) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *Macromolecules* **1979**, *12*, 1207.
(22) We are indebted to Drs. J. R. Falender and J. Saam of the Dow Corning Corp. for providing the PDMS polymer and the siloxane cross-linking agents, and information on their properties.
(23) Smith, A. L. "Analysis of Silicones"; Wiley-Interscience: New York, 1974.
(24) Mark, J. E.; Flory, P. J. *J. Appl. Phys.* **1966**, *37*, 4635.
(25) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(26) Flory, P. J.; Tatara, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 683.
(27) Mooney, M. *J. Appl. Phys.* **1948**, *19*, 434. Rivlin, R. S. *Philos. Trans. R. Soc. London, Ser. A* **1948**, *241*, 379.
(28) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(29) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.
(30) Flory, P. J. *Polymer* **1979**, *20*, 1317.
(31) Erman, B.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1115.
(32) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(33) K. O. Meyers and E. W. Merrill have also prepared and studied PDMS networks of high functionality (*Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **1980**, *21* (*1*), 213). Their results are difficult to interpret, however, since these experiments were apparently reproducible only to within a factor of approximately two.

Measurement of Polydispersity of Narrow Fractions and Column Spreading Parameters by Recycle Liquid Size Exclusion Chromatography

Frank L. McCrackin and Herman L. Wagner*

Polymer Science and Standards Division, National Bureau of Standards, Washington, D.C. 20234. *Received November 29, 1979*

ABSTRACT: A method has been developed, employing recycle size exclusion chromatography (GPC), to separate instrumental spreading from spreading due to the molecular weight distribution of the polymer. This is particularly important for polymers with small M_w/M_n values, such as the anionic polystyrenes, where instrumental spreading accounts for a large fraction of the total spreading. Because of interferences with the base line from impurities, a novel technique for treating the data was employed to minimize the effect of base line irregularities. The analysis separated the components of instrumental spreading into spreading due to the sample injection, σ_i, to the columns, σ_c, and to the pump and additional tubing needed for recycling, σ_p. A total of six anionic polystyrenes, including two Standard Reference Materials, SRM 705 and 1478, ranging in molecular weight from 9000 to 390 000 were analyzed in toluene and four in THF to give M_w/M_n values of 1.003–1.05. The value of σ_c increases with increasing molecular weight. In previous treatments of recycling, σ_i and σ_p were neglected, leading to less accurate values of M_w/M_n and σ_c.

The width of a peak in a liquid size exclusion chromatogram (LSEC) is due to the polydispersity of the polymer, the column spreading, and the spreading produced by injecting the polymer sample in a finite volume of solvent. For polymers with broad molecular weight distributions, the spreading due to the polydispersity of the polymer is much larger than the other components of the spreading which may therefore usually be neglected as a first approximation, and the molecular weight averages, M_w and M_n, and the polydispersity, M_w/M_n, may be computed from the chromatogram. However, for narrow fractions, the spreading due to the columns may not be neglected because it is large in relation to that due to the polydispersity of the fraction. Waters[1] and Grubisic-Gallot et al.[2] have used recycle chromatography to measure the polydispersity of narrow fractions, taking into account only the column spreading. In this treatment, we also include the spreading due to the injection as well as the additional spreading due to the pump and associated tubing required in recycle chromatography. The polydispersity, M_w/M_n, of narrow fractions may be more accurately measured by recycle chromatography than calculated from M_w and M_n

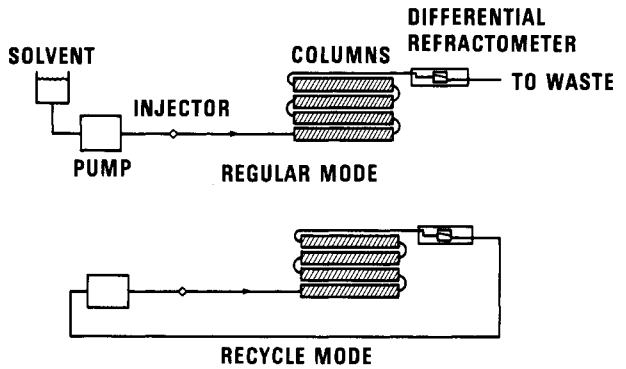

Figure 1. Schematic diagrams of the size exclusion chromatograph in regular and recycle modes.

measured separately by classic methods such as light scattering and osmotic pressure.

Once the polydispersity of a narrow fraction has been ascertained, it is possible with this narrow fraction to measure the column spreading for any given column set. This set may then be employed to measure the polydispersity of other narrow fractions, since the column spreading is now known.

Recycle Theory

The chromatograms of narrow fractions may usually be adequately approximated by Gaussian curves. The analysis of skewed chromatograms is treated later in this paper. The spreading of a chromatogram is measured by the dispersion defined by

$$\sigma^2 = \int (v - v_0)^2 H(v)\, dv / \int H(v)\, dv \qquad (1)$$

where $H(v)$ is the height of the chromatogram at the retention volume, v, and v_0 is the retention volume at the maximum height of the chromatogram. As indicated above, for a single pass of the fraction through the column this dispersion has three components: the dispersion due to column spreading, σ_c, the dispersion due to polydispersity of the polymer fraction, σ_d, and the dispersion produced by injecting the sample in a finite volume of solvent, σ_i. Because the squares of the dispersions are additive,[3] the squared dispersion is given by

$$\sigma_1^2 = \sigma_c^2 + a^2\sigma_d^2 + \sigma_i^2 \qquad (2)$$

where a is the slope of the calibration curve of the column given by

$$v = B - a \ln M \qquad (3)$$

If the calibration curve is not linear in ln M over the entire molecular weight range, it can still be well approximated by eq 3 for the narrow range of molecular weights in the fraction.

Figure 1 shows the chromatograph connected in the recycle mode. After the polymer sample passes through the differential refractometer in the first cycle, it continues through additional tubing and through the pump. Then it is recycled through the columns. Figure 2 shows schematically a typical chromatogram.

At each cycle, the dispersion of the chromatogram is increased due to dispersion of the column and due to polydispersity of the polymer sample. Also, a dispersion, σ_p, is added when the polymer sample passes through the extra tubing and pump from the differential refractometer to the injector. The dispersion, σ_n, of the chromatogram measured by the differential refractometer after passing through the column n times is given by

$$\sigma_n^2 = n\sigma_c^2 + n^2a^2\sigma_d^2 + \sigma_i^2 + (n-1)\sigma_p^2 \qquad (4)$$

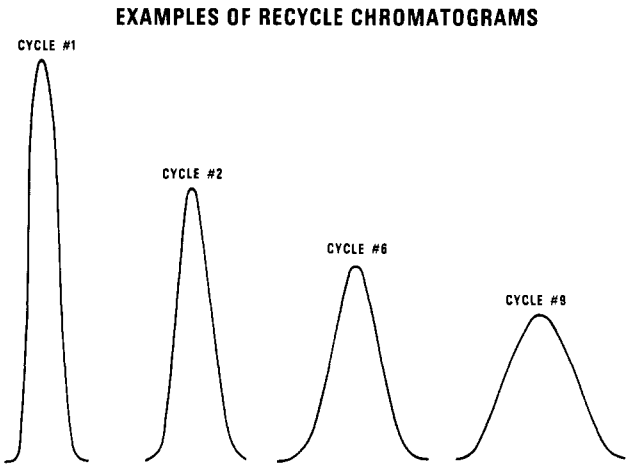

Figure 2. An idealized recycle chromatogram.

A mathematical derivation of eq 4 is given in Appendix I, but it may be easily interpreted. The dispersion, σ_c, due to the column is a random process due to a polymer molecule moving through the column with speeds faster or slower than its mean speed, so the contribution of this component to the squared dispersion will be the squared dispersion due to a single pass through the columns multiplied by the number of cycles, i.e., the component will be $n\sigma_c^2$. However, the contribution due to the polydispersity of the molecular weights in the sample will be proportional to n so that the contribution to the total squared dispersion will be proportional to n^2, or $n^2a^2\sigma_d^2$. The dispersion σ_i is produced by the single initial injection of the sample and does not increase with recycling, so its contribution to the total dispersion does not depend on n. The dispersion, σ_p, due to the sample passing through the extra tubing and pump is again a random process, so its contribution to the total squared dispersion will be proportional to $n - 1$, the number of times that the sample passes through the tubing and pump. The total squared dispersion of the chromatogram for cycle n is therefore given by eq 4 as the sum of the four components of the squared dispersion.

The dispersion, σ_d, due to the polydispersity of the polymer fraction is shown in Appendix I to be related to the polydispersity by:

$$\sigma_d^2 = \ln (M_w/M_n) \qquad (5)$$

Chromatograms were also measured in the recycle mode with the columns removed and the injection port connected directly to the differential refractometer. In this case, the dispersions due to the columns and the sample polydispersity are absent so that eq 4 reduces to

$$\sigma_n^2 = \sigma_i^2 + (n-1)\sigma_p^2 \qquad (6)$$

The method of analysis of the recycle chromatograms is now given. First, chromatograms were obtained for the chromatograph connected in the recycle mode with the columns removed and the dispersions of the chromatograms, σ_n, measured vs. cycle number, n. A graph of σ_n^2 vs. $n - 1$ was then drawn. By eq 6 a straight line is obtained and the values of σ_i^2 and σ_p^2 were determined as the intercept and slope, respectively, of the line.

Rearranging eq 4 gives

$$\frac{\sigma_n^2 - \sigma_i^2 - (n-1)\sigma_p^2}{n} = \sigma_c^2 + na^2\sigma_d^2 \qquad (7)$$

From a chromatogram of a polymer sample run on the recycle mode (Figure 1), the dispersion, σ_n, is measured

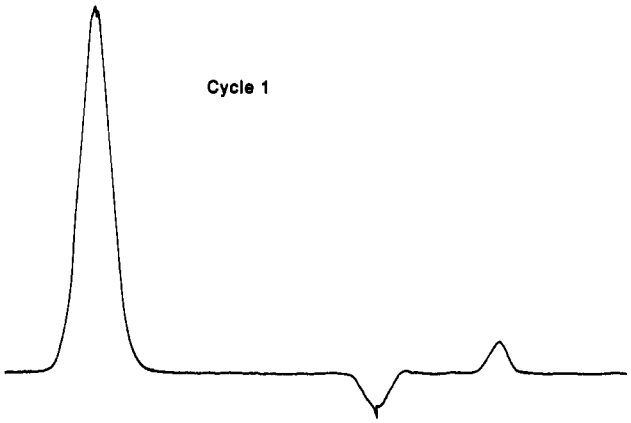

Figure 3. An acutal chromatogram for the first cycle.

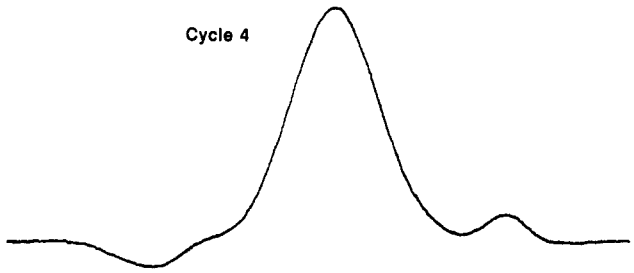

Figure 4. An actual chromatogram for a large cycle number.

vs. cycle number, n. Then the left-hand side of eq 7 is evaluated by using the previously determined values of σ_i and σ_p. This quantity plotted vs. n will, by eq 7, give a straight line with an intercept of σ_c^2 and a slope of $a^2\sigma_d^2$. The polydispersity of the polymer sample is then calculated from σ_d^2 by eq 5 by using a value of a determined from the calibration curve of the column.

Experimental Section

These measurements were carried out on a high-speed, high-performance LSEC system which consists of the following Waters Associates[6] components: (a) a high pressure pump, 6000A, in which flow rate is specified uniform to within 1% at 1 mL/min; (b) four microstyragel columns, 30 cm long, about 8 mm in diameter, with nominal pore sizes of 10^3, 10^4, 10^5, and 10^6 Å; (c) a U6K injector (septumless); and (d) an R401 differential refractometer as a detector. At the most sensitive gain we employed, full scale corresponded to about 1×10^{-4} refractive index units.

Both THF and toluene were used as solvents. Calibration of the columns was accomplished with narrow distribution polystyrenes, many of which were the samples analyzed in this work. For THF the calibration curve of retention volume vs. log molecular weight was linear. There was a small amount of curvature in the toluene calibration curve, but for the purpose of determining M_w/M_n, the value of the slope in the molecular weight region of interest was calculated and assumed constant over the narrow molecular weight range of the sample.

The narrow molecular weight distribution polystyrenes were obtained from the Pressure Chemicals Co., Pittsburgh, Pa.[6] Two NBS Standard Reference Materials, SRM's, were included: SRM 705, molecular weight about 180 000, and SRM 1478, molecular weight about 37 000.[4] Sample size was always 0.5 mL, with concentrations ranging from 0.1% for the highest molecular weight to 0.25% for the lowest.

The largest source of error in these recycle experiments is due to spurious peaks in the chromatograms that are not produced by the injected polymer. They are often ascribed to solvent impurities or air dissolved in the solvent. They are found at such low molecular weights that they are readily separated from the peak due to the polymer in the first cycle, as illustrated in Figure 3. However, on subsequent cycles, these extraneous peaks can occur on or near the polymer peak as shown in Figure 4, resulting in a distorted chromatogram and making it difficult to draw an accurate base line. These peaks were reduced in the case of toluene by flushing the injector with solvent before injection. In the case of THF, it was necessary to divert the flow to waste when these disturbances passed the refractometer in the first cycle, thus removing the components from the system. The system was then returned to the recycle mode. However, some distortion of the base line still occurs due to switching the flow from the recycle mode to waste and back again.

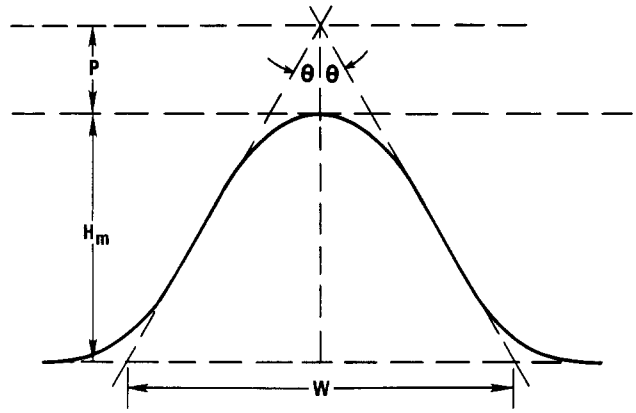

Figure 5. Measurements made on a chromatogram to determine its dispersion by the tangent and constant area methods.

Table I
Recycle Chromatograms of Polystyrene SRM 1478 in Toluene

cycle no. n	W, mL	H_m, cm	A, mL/cm	P, cm	W_{calcd}, mL	σ_n^2/n, mL^2
1	2.2	32.61	45.0	5.89	2.16	0.292
2	3.7	18.49	42.9	3.10	3.71	0.430
3	5.12	13.46	43.2	2.34	5.12	0.546
4	6.17	10.82	41.9	2.08	6.26	0.612
5	7.39	9.04	41.9	1.65	7.49	0.702
6	8.44	7.70	40.6	1.32	8.67	0.783
7	9.52	6.76	40.4	1.35	9.82	0.861
8	10.72	6.30	42.4	1.14	10.82	0.914
9	11.56	5.54	40.1	1.04	11.95	0.992

The dispersions were first calculated by using eq 1 and evaluating the integrals numerically. The results were highly dependent on the base line used, especially for chromatograms after a large number of cycles. This is because the integrals in eq 1 are very dependent on the tails of the chromatograms, and the tails may be badly distorted by spurious peaks. The dispersions were then determined from the widths of the chromatograms illustrated in Figure 5. The width of the chromatogram, W, is equal to 4σ, assuming the chromatogram is a Gaussian curve. The width is not as sensitive to the tails of the chromatogram and gives more consistent values for the dispersions than did numerical integration.

A large source of error in determining the dispersions is due to the uncertainty of the base line of the chromatograms for large values of n. A method that is independent of the base line was therefore devised, based on the areas of the chromatograms.

The area of a chromatogram, approximated by a Gaussian curve, is

$$A = (\pi/8)^{1/2} W H_m \tag{8}$$

where H_m, shown on Figure 5, is the maximum height of the chromatogram. Table I shows values of W, H_m, and A vs. cycle number, n, for a recycle chromatogram of SRM 1478. The computed area is seen to decrease with n, except for the first few cycles. However, the area is proportional to the amount of polymer in the sample, so it must be independent of the cycle number. The decrease of the calculated area occurs because the tails of the chromatograms fade into the background noise, due to the broadening of the chromatograms with n and the distortion from the spurious peaks. As a result, the base line is drawn too high, giving too small values for W, H_m, and the calculated areas.

To reduce this error, W was calculated on the assumption that the areas of the chromatograms are constant. Because the base

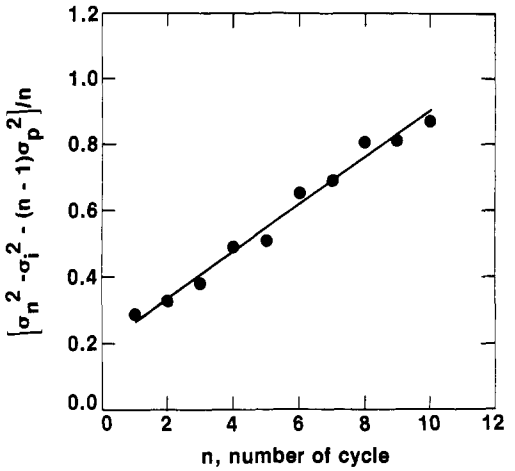

Figure 6. Graph for SRM 1478 (run 1) in toluene. The intercept gives the value of σ_c^2 and the polydispersity is calculated from the slope of the line.

line is more certain for the initial chromatograms, a value of 43 mL/cm is assumed for the area in this case. In addition to W and H_m, the distance P between the peak and the intersection of the tangents is also measured for each chromatogram. Then $\tan\theta$ is calculated as

$$\tan\theta = W/[2(P + H_m)] \quad (9)$$

H_m is eliminated from eq 8 and 9 and the result is solved for W to give

$$W_c = P\tan\theta + [P^2\tan^2\theta + 2(8/\pi)^{1/2}A\tan\theta]^{1/2} \quad (10)$$

Assuming A = 43 mL/cm, values of W_c were calculated by eq 10 for each cycle and are shown in Table I. These values depend only on the value of P and $\tan\theta$ of the chromatogram and are thus independent of the base line.

The chromatograms obtained in the recycle mode with the columns removed from the chromatograph were first analyzed. The squared dispersions, σ_n^2, of 0.056 and 0.302 mL^2 were obtained for the first and second cycles. By eq 6 we obtain

$$\sigma_i^2 = 0.056\ \text{mL}^2 \qquad \sigma_p^2 = 0.246\ \text{mL}^2 \quad (11)$$

The dispersion, σ_i, due to plug shape injection of the polymer sample is[3]

$$\sigma_i^2 = (\Delta v)^2/12 \quad (12)$$

where Δv is the volume of polymer solution injected. In practice, 0.5 mL of polymer solution was injected into a sample loading loop with a volume of 2 mL that initially contains solvent. The loop is then connected to the flow system, during which the 2 mL of solution and solvent from the loop flowed to the columns. If no mixing of the polymer solution and solvent occurs in the loop, then Δv is 0.5 mL and σ_i^2 = 0.021 mL^2. On the other hand, if complete mixing of the polymer solution and solvent occurs in the loop, Δv = 2 mL, the volume that flows from the loop to the columns, so σ_i^2 = 0.33 mL^2. The observed value of σ_i^2 of 0.056 mL^2 is between these extreme values, so partial mixing of the polymer solution and solvent in the loop appears to occur.

Chromatograms were also measured with the loop connected to the chromatograph for only 0.5 min so that only 0.5 mL of the solution flowed to the columns, giving Δv = 0.5 mL. These chromatograms gave the predicted value of σ_i^2 = 0.021 mL^2.

The dispersion σ_p is due to mechanical mixing of the polymer on passing through the connecting tube and the pump. Thus it is independent of the molecular weight of the polymer, and the value σ_p^2 = 0.246 mL^2 was used for analyzing all runs.

Results

Figure 6 shows the result for a recycle run of SRM 1478 in toluene. The total dispersions of the chromatograms, σ_n, were measured as previously described for cycles n = 1–10. The quantity $[\sigma_n^2 - \sigma_i^2 - (n-1)\sigma_p^2]/n$ was calculated for each cycle and is plotted in Figure 6 vs. n. The data

Table II
Polydispersities and Column Spreading Parameters for Polystyrene Samples

sample	solvent	$M \times 10^{-3}$	M_w/M_n	σ_c, mL
SRM 1477	toluene	9.1	1.124	0.259
	THF		1.050	0.158
SRM 1478	toluene	36	1.0095	0.395
	toluene		1.0099	0.436
	toluene		1.0091	0.437
	THF		1.0090	0.394
PC25170	toluene	51	1.0028	0.336
PC4b	toluene	111	1.0030	0.581
	toluene		1.0043	0.449
SRM 705[a]	toluene	175	1.0062	0.592
	THF		1.0090	0.505
PC50124	toluene	233	1.0028	0.551
PC3b	toluene	390	1.0027	0.538

[a] Values for only the large peak in the chromatogram.

are seen to fit a straight line with intercept and slope of 0.190 and 0.071, respectively. By comparison with eq 7,

$$\sigma_c^2 = 0.190 \qquad a^2\sigma_d^2 = 0.071 \quad (13)$$

The molecular weight of the polymer sample SRM 1478 is 3.6×10^4. The slope, a, of the calibration curve of these columns for polystyrene of molecular weight of 3.6×10^4 is −2.68. These values of σ_d^2 and a were substituted in eq 5 and the equation solved to give

$$M_w/M_n = 1.010 \quad (14)$$

Thirteen recycle runs were performed with seven polystyrenes. The results are shown in Table II.

The chromatogram of SRM 705 consisted of a large peak and a small distinct shoulder at a higher molecular weight that is believed to be due to the presence of some polymer of about twice the molecular weight of the bulk of the polymer. The measurements on the chromatogram were made on only the large peak, so that the measured polydispersities are for only that part of the polymer. The polydispersity of SRM 705 is thus larger than the values given in Table II.

These results are not in disagreement with those certified for SRM 705 and SRM 1478, as is evident from the precision assigned to the molecular weight given on the certificates[4] for these polymers.

Skewness

The chromatograms were approximated as symmetrical Gaussian curves in the preceding analysis. However, since skewed chromatograms are sometimes obtained, the analysis is extended to include skewing.

The skewness of a chromatogram is defined by

$$S_n = \frac{\int (v - v_0)^3 H(v)\, dv}{\int H(v)\, dv} \quad (15)$$

where v_0 is the mean retention volume. The skewness is caused by the skewness of the molecular weight distribution of the polymer and a skewed column dispersion. The skewness for the chromatogram at the nth cycle is shown in Appendix II to be given by

$$S_n/n = {}^2/_{27}w^3 - {}^2/_{27}a^3y^3n^2 \quad (16)$$

where w and y, defined in Appendix II, are measures of the skewness of the column dispersion and polymer molecular weight distribution, respectively. The two components of the skewness may be evaluated. First, S_n is computed by eq 15 for a number of cycles. Then S_n/n plotted vs. n^2 gives a straight line by eq 16. The measure,

w, of the skewness of the column dispersion is computed from the intercept of the line, and the measure, y, of the skewness of the polymer molecular weight distribution is computed from the slope of the line.

The dispersion, σ_c, of the column spreading and σ_x of the MWD are next computed by rearranging eq II.7 to give

$$\frac{\sigma_n^2 - \sigma_i^2 - (n-1)\sigma_p^2 - \frac{2}{9}a^2y^2n^2 - \frac{2}{9}w^2n}{n} = \sigma_c^2 + na^2\sigma_x^2 \tag{17}$$

The left-hand side of eq 17 is computed by using values y and w from the analysis of skewing and σ_i and σ_p computed from measurement with the columns removed. The values σ_c^2 and σ_x^2 are then determined from the slope and intercept of a plot of the left-hand side of eq 17 vs. n.

As shown in Appendix II, the ratios of molecular weight averages are given by

$$\frac{M_w}{M_n} = \frac{5 + 2e^y + 2e^{-y}}{9}\exp(\sigma_x^2) \tag{18}$$

and

$$\frac{M_z}{M_w} = 3\frac{2 + e^{2y}}{(2 + e^y)^2}\exp(\sigma_x^2) \tag{19}$$

Therefore, the analysis of both the skewness and dispersion of the chromatograms yields the molecular weight ratio M_z/M_w in addition to the polydispersity, M_w/M_n, of the MWD of the polymer. However, the interference of the spurious peaks on the chromatograms caused the values of S_n calculated by eq 15 to be too inaccurate for a reliable analysis of the skewness to be performed. Hopefully, these spurious peaks will be removed in future LSEC investigations so that the above analysis of the skewness will be feasible.

Discussion

The values of the polydispersity M_w/M_n vary from about 1.003 to about 1.01. The precision may be determined from the replication of recycle runs for samples SRM 1478, PC4b, and SRM 705 as shown in Table II. The values of M_w/M_n for SRM 1478 show excellent agreement, while the values for PC4b and SRM 705 also show good agreement. These results indicate that these materials are very narrow in molecular weight distribution.

Because account is taken of the spreading due to the sample injection and the pump, σ_i and σ_p, it is possible to obtain more reliable values of the column spreading parameter, σ_c, than heretofore. If it is assumed, as has been done previously, that the total spreading is due only to the columns and the polydispersity of the sample, then by eq 7, $\sigma_n^2/n = \sigma_c^2 + na^2\sigma_d^2$. Thus a plot of σ_n^2/n vs. n should yield a straight line with a value of σ_c^2 from the intercept and σ_d^2 from the slope. This is the method used by Grubisic-Gallot et al.[2] Such a plot of some of our data is shown by the triangles in Figure 7, together with the same data, plotted by squares, as before corrected for σ_i and σ_p. It is evident that in the former treatment a straight line is not obtained and the plot shows distinct curvature.

If the points for low values of n are ignored, the slope of a line through the points gives an approximate value of $a^2\sigma_d^2$, from which the polydispersity of the sample may be calculated. However, $a^2\sigma_d^2$ may be more accurately calculated from the data, shown by the squares, corrected for σ_i and σ_p. A reliable value for σ_c^2 may not be obtained from the uncorrected values.

Waters[1] plotted a quantity proportional to σ_n^2/n vs. $1/n$. He did not correct for σ_i and σ_p, so his method is also only approximate.

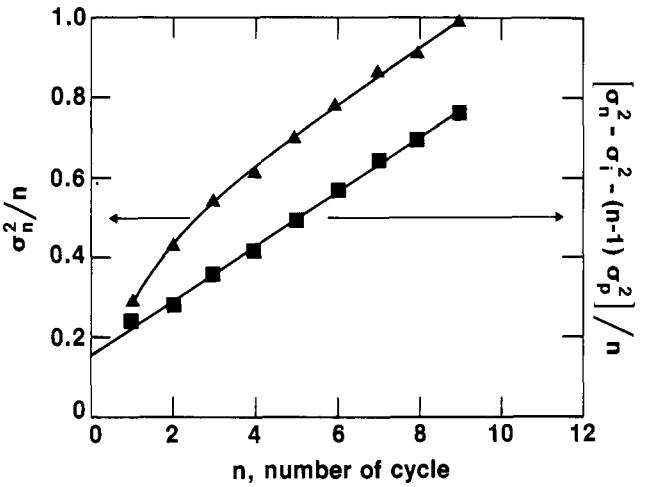

Figure 7. Graph for SRM 1478 in toluene (run 2). Data plotted as $[\sigma_n^2 - \sigma_i^2 - (n-1)\sigma_p^2]/n$: (■) as in Figure 6, and as σ^2/n (▲).

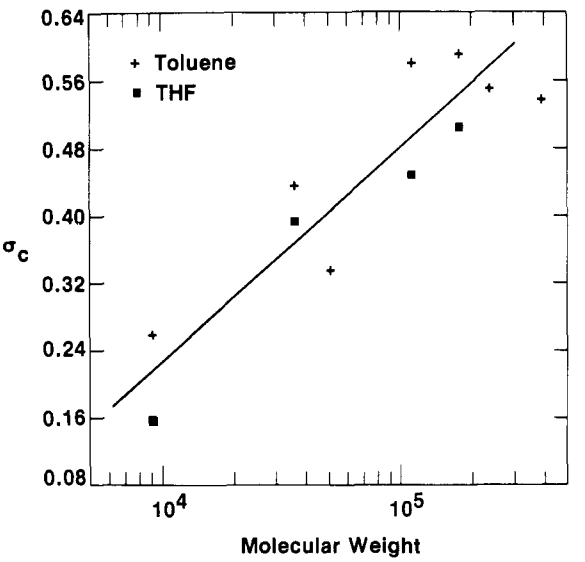

Figure 8. Column spreading vs. molecular weight of sample.

Figure 8 shows σ_c vs. molecular weight of the samples. The column spreading is seen to increase with molecular weight and does not depend on solvent. Tung[5] found that σ_c was also independent of polymer. However, he found a maximum in σ_c with respect to molecular weight (a minimum in his value of h) for his column set, which is not found in our data.

Conclusions

By taking into account the dispersion due to the injection of the sample and the dispersion due to the pump, it has been possible to obtain accurate values of the polydispersity of narrow molecular weight distribution polystyrenes. Because of the special technique employed to analyze the chromatograms, irregularities in the base line caused by solvent impurities have been minimized. These samples have much narrower molecular weight distributions than previously suspected. Now that their M_w/M_n values are known, they may be employed to estimate the column spreading of any other column set.

Appendix I. Derivation of Dispersion of Recycle Size Exclusion Chromatograms

Recycle SEC is best analyzed[3] by Laplace transforms. The input function, the shape at injection, may be represented by a Gaussian curve, and the spreading functions of the column and the pump and piping from the detector

and the head of the column may also be represented by Gaussian curves. The transform of the chromatogram of a monodisperse polymer at the detector is given by the product of the transforms of the input function and the spreading functions. On taking the inverse transform, the chromatogram after the sample passed through the column n times is proportional to

$$\exp\{-[v - nv_0 - (n-1)v_p]^2/2[n\sigma_c^2 + \sigma_i^2 + (n-1)\sigma_p^2]\} \quad (I.1)$$

where v_0 is the retention time of the column, v_p is the retention time of the pump and tubing, and σ_c, σ_i, and σ_p are the dispersions of the column, injection, and pump and tubing, respectively.

Equation I.1 applies to a monodisperse polymer. The retention volume, v_0, of the peak of the chromatogram is given by eq 3 as

$$v_0 = B - aX \quad (I.2)$$

where

$$X = \ln M \quad (I.3)$$

and M is the molecular weight of the polymer. The polymer sample is assumed to have a narrow logarithmic-normal molecular weight distribution given by

$$F(X) = \exp[-(X - \bar{X})^2/2\sigma_d^2] \quad (I.4)$$

The chromatogram H_n for this molecular weight distribution is obtained by substituting eq I.2 in eq I.1 and integrating over the molecular weight distribution eq I.4

$$\begin{aligned} H_n \propto \int_{-\infty}^{\infty} &\exp[-(X - \bar{X})^2/2\sigma_d^2] \times \\ &\exp\{-[v - nB + na\bar{X} - (n-1)v_p]^2/ \\ &\quad 2[n\sigma_c^2 + \sigma_i^2 + (n-1)\sigma_p^2]\}\, dx \\ \propto &\exp\{-[v - nB + na\bar{X} - (n-1)v_p]^2/ \\ &\quad 2[n\sigma_c^2 + \sigma_i^2 + (n-1)\sigma_p^2 + n^2a^2\sigma_d^2]\} \quad (I.5) \end{aligned}$$

The chromatogram is therefore a Gaussian curve and its dispersion is

$$\sigma_n^2 = n\sigma_c^2 + \sigma_i^2 + (n-1)\sigma_p^2 + n^2a^2\sigma_d^2 \quad (I.6)$$

The weight average molecular weight for the distribution I.11 is given by

$$M_w = \frac{\int_{-\infty}^{\infty} MF(X)\, dX}{\int_{-\infty}^{\infty} F(X)\, dX} = \exp(\bar{X} + \sigma_d^2/2) \quad (I.7)$$

where M from eq I.3 and $F(X)$ from eq I.4 are substituted and integrations performed. Similarly,

$$M_n = \exp(\bar{X} - \sigma_d^2/2) \quad (I.8)$$

Solving eq I.7 and I.8 for σ_d^2 gives

$$\sigma_d^2 = \ln (M_w/M_n) \quad (I.9)$$

Appendix II. Derivation of Dispersion and Skewness of Recycle Size Exclusion Chromatograms

The chromatogram of a monodisperse polymer after passing through the columns is assumed to be proportional to

$$\exp[-(v - v_0)^2/2\sigma_c^2] + f\exp[-(v - v_0 - w)^2/2\sigma_c^2] \quad (II.1)$$

instead of the single Gaussian curve given by eq I.1. The larger the values of f and w, the more skewed is the chromatogram. If $f = 0$ or $w = 0$, the chromatogram reduces to a single symmetrical Gaussian curve.

The molecular weight distribution of the polymer is also assumed to be skewed and to be given by

$$\exp[-(X - \bar{X})^2/2\sigma_x^2] + b\exp[-(X - \bar{X} - y)^2/2\sigma_x^2] \quad (II.2)$$

By a computation similar to that in Appendix I, we derive

$$v_n = \left(B - a\bar{X} - \frac{bay}{1+b} + \frac{wf}{1+f}\right)n + v_p(n-1) \quad (II.3)$$

$$\sigma_n^2 = \sigma_i^2 + n\sigma_c^2 + (n-1)\sigma_p^2 + n^2a^2\sigma_x^2 + \frac{ba^2y^2}{(1+b)^2}n^2 + \frac{w^2f}{(1+f)^2}n \quad (II.4)$$

$$S_n = \frac{w^3f(1-f)}{(1+f)^3}n + \frac{a^3y^3b(f-1)}{(1+b)^3}n^3 \quad (II.5)$$

The skewing depends on the parameters f, w, b, and y of eq II.1 and II.2. Because it is impossible to determine all four parameters from experimental chromatograms, we treat the case that $f = b = 1/2$. In this case eq II.3–II.5 give

$$v_n = (B - a\bar{X} - 1/3ay + w/3)n + v_p(n-1) \quad (II.6)$$

$$\sigma_n^2 = \sigma_i^2 + n\sigma_c^2 + (n-1)\sigma_p^2 + n^2a^2\sigma_x^2 + \tfrac{2}{9}a^2y^2n^2 + \tfrac{2}{9}w^2n \quad (II.7)$$

$$S_n = \tfrac{2}{27}w^3n - \tfrac{2}{27}a^3y^3n^3 \quad (II.8)$$

For the ratios of molecular weight averages we obtain

$$\frac{M_w}{M_n} = \frac{5 + 2\exp(y) + 2\exp(-y)}{9}\exp(\sigma_x^2) \quad (II.9)$$

$$\frac{M_z}{M_w} = \frac{3(2 + \exp(2y))}{(2 + \exp(y))^2}\exp(\sigma_x^2) \quad (II.10)$$

References and Notes

(1) J. L. Waters, *J. Polym. Sci., Part A-2*, **8**, 411 (1970).
(2) Z. Grubisic-Gallot, L. Marais, and H. Benoit, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 959 (1976).
(3) J. C. Sternberg, *Adv. Chromatogr.*, **2**, 205 (1966).
(4) NBS Certificate SRM 705 and SRM 1478. Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.
(5) L. H. Tung and J. R. Runyon, *J. Appl. Polym. Sci.*, **13**, 2397 (1969).
(6) Certain commercial materials and instruments are identified in this paper in order to adequately specify the experiment procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards.