Journal of Chromatography, 322 (1985) 338–346
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,566

Note

Molecular weight determination of polychromophore polymers using high-performance liquid chromatography and size-exclusion chromatography with UV detection

SHIH-TSE LAI* and LOUIS SANGERMANO
Rockwell International, Semiconductor Products Division, Analytical Laboratory, MS 503-210, Newport Beach, CA 92660 (U.S.A.)
(Received December 21st, 1984)

In size-exclusion chromatography (SEC), an equal detector response to components of different molecular weight is of significance for accurate molecular weight measurement of polymers. The consideration of UV absorbance in accordance with the numbers of chromophore per molecule has confined the applicability of UV detector only to polymers with a single double bond or similar chromophore per molecule for solute detection[1]. The same reason has led to the development of a chromatogram-peak-area correction method of molecular weight determination for styrene oligomers[2] and epoxy novolac oligomers[3] using chemically-bonded phase high-performance liquid chromatography (HPLC).

In this contribution, we will demonstrate that the molecular weight distribution curve of polystyrene polymers obtained from SEC with UV detection can be corrected and used for the determination of molecular weight. Both HPLC and SEC results indicate the molecular weight (MW) deviation in between the uncorrected and corrected values decreases as the MW of the sample increases.

EXPERIMENTAL

HPLC

The chromatographic system included a Perkin-Elmer series 3B microcomputer-controlled pump module, a Beckman 165 variable-wavelength detector, and a Perkin-Elmer Sigma 10B chromatography data station. The UV detector was set at a wavelength of 260 nm. A 25 cm × 4.6 mm Excaliber Spherisorb S5P (5 μm) phenyl-bonded phase column (Applied Science) was used for the separation.

SEC

The SEC system included a Waters Assoc. 6000A solvent delivery system, a Perkin-Elmer LC 75 spectrophotometric detector, a HP 85 microcomputer and Nelson Analytical GPC software. The column set included four Waters Assoc. ultra styragel columns (500 Å, 10^3 Å, 10^4 Å and 10^5 Å). The mobile phase was tetrahydrofuran (THF) at 1 ml/min. The UV detector was set at 260 nm.

0021-9673/85/$03.30

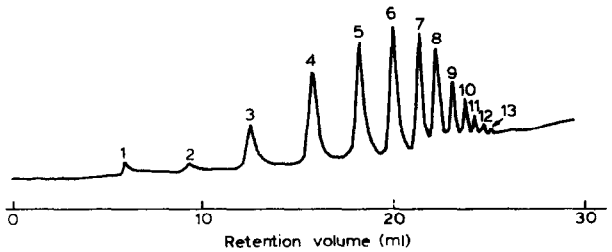

Fig. 1. Gradient elution of PS 580, starting from THF–water (50:50) to 100% THF in 30 min with a concave curvature of 2. The degree of polymerization (n) of oligomer peak is indicated in the figure.

Standards

A Perkin-Elmer polystyrene standard kit (ranging from 600 to $1.46 \cdot 10^6$) was used to determine the SEC molecular weight distribution curve. The PL polystyrene standards (580, 1050, 1350 and 1770) were also used in the experiment.

RESULTS AND DISCUSSION

Our previous work showed that styrene oligomers can be separated on a phenyl-bonded phase column using either THF–hexane[4] or THF–water[5] eluents. Fig. 1 illustrates a base-line separation chromatogram of low-MW styrene oligomers PS 580 using phenyl-bonded phase HPLC with UV detection at a wavelength of 260 nm. For a sample of monochromophore, the number averaged molecular weight (M_n), weight averaged molecular weight (M_w) and z averaged molecular weight (M_z) can be expressed as

$$M_n = \frac{\Sigma M_i A_i}{\Sigma A_i} \tag{1}$$

$$M_w = \frac{\Sigma M_i^2 A_i}{\Sigma M_i A_i} \tag{2}$$

$$M_z = \frac{\Sigma M_i^3 A_i}{\Sigma M_i^2 A_i} \tag{3}$$

where M_i and A_i are the increment of molecular weight and area, respectively. For a sample of polychromophore such as styrene oligomers, the area corresponding to the individual oligomer peak has to be corrected in order to represent the actual amount of molecules. The corrected area can be written as eqn. 4.

$$A_i' = \frac{A_i}{n} \tag{4}$$

where A_i' is the corrected area and n is the degree of polymerization. Tables I–IV list the results of uncorrected and corrected values of M_n, M_w, M_z, and polydispersity (M_w/M_n) of polystyrene standards (PS 580, 1050, 1350 and 1770). As indicated in

TABLE I

MOLECULAR WEIGHT CALCULATION OF PS 580

Polydispersity value (M_w/M_n) supplied by manufacturer = 1.14; $M_i = 58 + 104\,n$; % deviation = |(uncorrected value − corrected value)|/corrected value.

n	A_i	A_i'	M_iA_i	M_iA_i'	$M_i^2A_i$	$M_i^2A_i'$	$M_i^3A_i$	$M_i^3A_i'$
1	0.0310	0.0310	5.0220	5.0220	813.5640	813.5640	131,797.368	131,797.368
2	0.0295	0.01475	7.8470	3.9235	2087.3020	1043.6510	555,222.332	277,611.166
3	0.2996	$9.98667 \cdot 10^{-2}$	110.8520	36.9507	41,015.2400	13,671.7470	15,175,638.800	5,058,546.267
4	0.6111	$1.52775 \cdot 10^{-1}$	289.6614	72.4154	137,299.5040	34,324.8760	65,079,964.706	16,269,991.177
5	0.7320	0.1464	423.0960	84.6192	244,549.4880	48,909.8976	141,349,604.064	28,269,920.813
6	0.6955	0.1159	474.3310	79.0552	323,493.7420	53,915.6237	220,622,732.044	36,770,455.341
7	0.5457	$7.79571 \cdot 10^{-2}$	428.9202	61.2743	337,131.2772	48,161.6110	264,985,183.879	37,855,026.268
8	0.3767	$4.70875 \cdot 10^{-2}$	335.2630	41.9079	298,384.0700	37,298.0088	265,561,822.300	33,195,227.788
9	0.2229	$2.47667 \cdot 10^{-2}$	221.5626	24.6181	220,233.2244	24,470.3583	218,911,825.054	24,323,536.117
10	0.1217	0.01217	133.6266	13.3627	146,722.0068	14,672.2007	161,100,763.466	16,110,076.347
11	0.0596	$5.41818 \cdot 10^{-3}$	71.6392	6.5126	86,110.3184	7828.2108	103,504,602.717	9,409,509.338
12	0.0270	$2.250 \cdot 10^{-3}$	35.2620	2.9385	46,052.1720	3837.6810	60,144,136.632	5,012,011.386
13	0.0167	$1.2846 \cdot 10^{-3}$	23.5470	1.8113	33,201.2700	2553.9438	46,813,790.700	3,601,060.823

Uncorrected	$M_n = 679.3924$	$M_w = 748.6803$	$M_z = 815.7856$	$(M_w/M_n) = 1.10985$
Corrected	$M_n' = 593.7480$	$M_w' = 671.0263$	$M_z' = 741.9683$	$(M_w'/M_n') = 1.13015$
% Deviation	14.4243	11.5724	9.9488	2.4924

TABLE II

MOLECULAR WEIGHT CALCULATION OF PS 1050

Polydispersity value (M_w/M_n) supplied by manufacturer = 1.20. The gradient elution conditions of Tables II, III and IV are a linear gradient elution starting from THF–water (50:50) to THF–water (65:25) in 40 min, then the elution maintains at THF–water (65:35) isocratic condition.

n	A_i	A_i'	M_iA_i	M_iA_i'	$M_i^2A_i$	$M_i^2A_i'$	$M_i^3A_i$	$M_i^3A_i'$
1	–							
2	0.0303	0.01515	8.0598	4.0299	2143.9068	1071.9534	570,279.2088	285,139.6044
3	0.2101	$7.00333 \cdot 10^{-2}$	77.7370	25.9123	28,762.6900	9587.5633	10,642,195.3000	3,547,398.4333
4	0.3760	0.09400	178.2240	44.5560	84,478.1760	21,119.5440	40,042,655.4240	10,010,663.8560
5	0.4715	0.09430	272.5270	54.5054	157,520.6060	31,504.1212	91,046,910.2682	18,209,382.0536
6	0.6744	0.11240	459.9408	76.6568	313,679.6256	52,279.9376	213,929,504.6590	35,654,917.4432
7	0.9383	0.13404	737.5038	105.3577	579,677.9868	82,811.1410	455,626,897.6250	65,089,556.8035
8	1.1668	0.14585	1038.4520	129.8065	924,222.2800	115,527.7850	822,557,829.2050	102,819,728.6500
9	1.3268	0.14742	1318.8392	146.5377	1,310,926.1648	145,658.4628	1,303,060,607.8100	144,784,511.9790
10	1.3889	0.13889	1525.0122	152.5012	1,674,463.3956	167,446.3396	1,838,560,808.3700	183,856,080.8370
11	1.3915	0.12650	1672.5830	152.0530	2,010,444.7660	182,767.7060	2,416,554,608.7300	219,686,782.6120
12	1.3021	0.10851	1700.5426	141.7119	2,220,908.6356	185,075.7196	2,900,506,678.1000	241,708,889.8420
13	1.1722	$9.01692 \cdot 10^{-2}$	1652.8020	127.1386	2,330,450.8200	179,265.4477	3,285,935,656.2000	252,764,281.2460
14	0.9982	0.07130	1511.2748	107.9482	2,288,070.0472	163,4333.5748	3,464,138,051.5000	247,438,432.3500
15	0.8532	0.05688	1380.4776	92.0318	2,233,612.7568	148,907.5171	3,613,985,440.5000	240,932,362.7000
16	0.7510	$4.69375 \cdot 10^{-2}$	1293.2222	80.8264	2,226,928.2840	139,183.0178	3,834,770,505.1000	239,673,156.5690
17	0.6288	$3.69882 \cdot 10^{-2}$	1148.1888	67.5405	2,096,592.7488	123,328.9852	3,828,378,359.3000	225,198,727.0180
18	0.4389	$2.43833 \cdot 10^{-2}$	847.0770	47.0598	1,634,858.6100	90,825.4783	3,155,277,117.3000	175,293,173.1830
19	0.4077	$2.14579 \cdot 10^{-2}$	829.2618	43.6453	1,686,718.5012	88,774.6580	3,430,785,434.4000	180,567,654.4420
20	0.2326	0.01163	497.2988	24.8649	1,063,224.8344	53,161.2417	2,273,174,696.0000	113,658,734.8000
21	0.2321	$1.10524 \cdot 10^{-2}$	520.3682	24.7794	1,166,665.5044	55,555.5002	2,615,664,060.9000	124,555,431.4710
22	0.1288	$5.85454 \cdot 10^{-3}$	302.1648	13.7348	708,878.6208	32,221.7555	1,663,029,244.4000	75,592,238.3818
23	0.0624	$2.71304 \cdot 10^{-3}$	152.8800	6.6470	374,556.0000	16,285.0435	917,662,200.0000	39,898,356.5200

Uncorrected	M_n = 1259.6286	M_w = 1417.9651	M_z = 1555.2856	(M_w/M_n) = 1.1257
Corrected	M_n' = 1065.9973	M_w' = 1249.0933	M_z' = 1410.1238	(M_w'/M_n') = 1.1718
% Deviation	18.1643	13.5196	10.2943	3.9308

TABLE III

MOLECULAR WEIGHT CALCULATION OF PS 1350

Polydispersity value (M_w/M_n) supplied by manufacturer = 1.07.

n	A_i	A'_i	M_iA_i	$M_iA'_i$	$M_i^2A_i$	$M_i^2A'_i$	$M_i^3A_i$	$M_i^3A'_i$
1	–							
2	–							
3	–							
4	–							
5	–							
6	–							
7	0.2112	$3.01714 \cdot 10^{-2}$	166.0032	23.7147	130,478.5152	18,639.7879	102,556,112.9470	14,650,873.2782
8	0.4059	$5.07375 \cdot 10^{-2}$	361.2510	45.1564	321,513.3900	40,189.1738	286,146,917.1000	35,768,364.6375
9	0.4504	$5.00444 \cdot 10^{-2}$	447.6976	49.7442	445,011.4144	49,445.7127	442,341,345.9140	49,149,038.4349
10	0.4683	0.04683	514.1934	51.4193	564,584.3532	56,458.4353	619,913,619.8190	61,991,316.9819
11	0.5213	$4.73909 \cdot 10^{-2}$	626.6026	56.9639	753,176.3252	68,470.5750	905,317,942.8900	82,301,631.1718
12	0.6252	0.05210	816.5112	68.0426	1,066,363.6272	88,863.6356	1,392,670,897.1200	116,055,908.0930
13	0.6653	$5.11769 \cdot 10^{-2}$	938.0730	72.1595	1,322,682.9300	101,744.8408	1,864,982,931.3000	143,460,225.4850
14	0.6891	$4.92214 \cdot 10^{-2}$	1,043.2974	74.5212	1,579,552.2636	112,825.1617	2,391,442,127.0900	170,817,294.7920
15	0.6777	0.04518	1,096.5186	73.1012	1,774,167.0948	118,277.8063	2,870,602,359.4200	191,373,490.6280
16	0.6130	$3.83125 \cdot 10^{-2}$	1,055.5860	65.9741	1,817,719.0920	113,607.4432	3,130,112,276.4000	195,632,017.2750
17	0.5159	$3.03470 \cdot 10^{-2}$	942.0334	55.4137	1,720,152.9884	101,185.4699	3,140,999,356.8000	184,764,668.0470
18	0.3597	$1.99833 \cdot 10^{-2}$	694.2210	38.5678	1,339,846.5300	74,435.9183	2,585,903,802.9000	143,661,322.3830
19	0.2472	$1.30105 \cdot 10^{-2}$	502.8048	26.4634	1,022,704.9632	53,826.5770	2,080,181,895.2000	109,483,257.6420
20	0.1462	0.00731	312.5756	15.6288	668,286.6328	33,414.3316	1,428,796,820.9000	71,439,841.0450
21	0.0652	$3.10476 \cdot 10^{-3}$	146.1784	6.9609	327,731.9728	15,606.2844	734,775,083.0000	34,989,289.6667

Uncorrected	M_n = 1450.6346	M_w = 1537.1138	M_z = 1614.1638	(M_w/M_n) = 1.0596
Corrected	M'_n = 1353.1569	M'_w = 1446.4564	M'_z = 1533.4787	(M'_w/M'_n) = 1.0689
% Deviation	7.2037	6.2676	5.2616	8.7326

TABLE IV

MOLECULAR WEIGHT CALCULATION OF PS 1770

Polydispersity value (M_w/M_n) supplied by manufacturer = 1.06.

n	A_i	A_i'	M_iA_i	M_iA_i'	$M_i^2A_i$	$M_i^2A_i'$	$M_i^3A_i$	$M_i^3A_i'$
1	–							
2	–							
3	–							
4	–							
5	–							
6	–							
7	–							
8	0.0456	0.00570	40.5840	5.0730	36,119.7600	4514.9700	32,146,596.4000	4,018,323.3000
9	0.0786	$8.73333 \cdot 10^{-3}$	78.1284	8.6809	77,659.6296	8628.84777	77,193,671.8220	8,577,074.6469
10	0.2437	0.02437	267.5826	26.7583	293,805.6948	29,380.5695	322,598,652.8900	32,259,865.2890
11	0.3454	0.03140	415.1708	37.7428	499,035.3016	45,366.8456	599,840,432.5280	54,530,948.41216
12	0.4532	$3.77667 \cdot 10^{-2}$	591.8792	49.3233	772,994.2352	64,416.1863	1,009,530,471.1700	84,127,539.2642
13	0.5937	$4.56692 \cdot 10^{-2}$	837.1170	64.3936	1,180,334.9700	90,794.9977	1,664,272,307.7000	128,020,946.7460
14	0.6692	0.04780	1013.1688	72.3692	1,533,937.5632	109,566.9688	2,322,381,470.6800	165,884,390.7630
15	0.8714	$5.80933 \cdot 10^{-2}$	1409.9252	93.9950	2,281,258.9736	152,083.9316	3,691,077,019.2800	246,071,801.2850
16	1.0088	0.06305	1737.1536	108.5721	2,991,378.4992	186,961.1562	5,151,153,775.6300	321,974,110.9770
17	1.0273	$6.04294 \cdot 10^{-2}$	1875.8498	110.3441	3,425,301.7348	201,488.3373	6,254,600,967.7000	367,917,703.9820
18	1.0508	$5.83778 \cdot 10^{-2}$	2028.0440	112.6691	3,914,124.9200	217,451.3844	7,554,261,095.6000	419,681,171.9780
19	1.0902	$5.73789 \cdot 10^{-2}$	2217.4668	116.7088	4,510,327.4712	237,385.6564	9,174,006,076.4000	482,842,425.0740
20	1.0046	0.05023	2147.8348	107.3917	4,592,070.8024	229,603.5401	9,817,847,375.5000	490,892,368.7750
21	0.7987	$3.80333 \cdot 10^{-2}$	1790.6854	85.2707	4,014,716.6668	191,176.9841	9,000,994,767.0000	428,618,798.4290
22	0.7540	$3.42727 \cdot 10^{-2}$	1768.8840	80.4038	4,149,801.8640	188,627.3574	9,735,435,172.9000	442,519,780.5860
23	0.5691	$2.47435 \cdot 10^{-2}$	1394.2950	60.6215	3,416,022.7500	148,522.7283	8,369,255,737.5000	363,880,684.2390
24	0.4296	0.01790	1097.1984	45.7166	2,802,244.7136	116,760.1964	7,156,932,998.5000	298,205,541.6040
25	0.5726	$2.29040 \cdot 10^{-2}$	1521.97088	60.8788	4,045,398.3864	161,815.9354	10,752,668,911.1000	430,106,756.4440

Uncorrected	M_n = 1915.5593	M_w = 2003.1780	M_z = 2081.1273	(M_w/M_n) = 1.0457
Corrected	M_n' = 1815.4027	M_w' = 1912.3594	M_z' = 2000.4236	(M_w'/M_n') = 1.0534
% Deviation	5.5170	4.7490	4.0343	0.0072785

TABLE V

MW DEVIATION *VS.* MW RANGE

The linear plot of log MW *vs.* elution volume (V_e) in Fig. 2B can be expressed as: log MW = 1.026 − 0.1891 V_e. D = Deviation.

V_e (ml)	M_n	M'_n	D %	M_w	M'_w	D %	M_z	M'_z	D %	P	P'	D %
25.9	208,212.6	184,556.8	12.817	229,497.7	208,205.3	10.227	249,615.7	229,491.9	8.769	1.1022	1.1281	2.30
26.4	167,477.7	148,448.1	12.819	184,598.6	167,470.4	10.228	200,780.6	184,592.8	8.769	1.1022	1.1281	2.30
26.9	134,712.2	119,403.6	12.821	148,483.6	134,704.9	10.229	161,499.7	148,477.8	8.770	1.1022	1.1281	2.30
27.4	108,357.0	96,041.5	12.823	119,434.1	108,349.7	10.230	129,903.8	119.428.3	8.771	1.1022	1.1281	2.30
27.9	87,157.9	77,249.9	12.826	96,097.9	87,150.6	10.232	104.489.3	96,062.1	8.773	1.1022	1.1281	2.30
28.4	70,106.3	62,134.8	12.829	77,273.1	70,098.9	10.234	84,046.9	77,267.3	8.774	1.1022	1.1282	2.30
29.4	45,358.3	40,197.4	12.839	49,995.2	45,351.0	10.241	54,377.8	49,989.4	8.779	1.1022	1.1282	2.302
30.4	29,346.5	26,003.9	12.854	32,346.6	29,339.2	10.250	35,182.1	32,340.7	8.786	1.1022	1.1283	2.31
31.4	18,987.0	16,820.9	12.877	20,928.0	18,979.7	10.265	22,762.6	20,922.2	8.796	1.1022	1.1283	2.313
32.4	12,284.5	10,879.5	12.913	13,540.3	12,277.1	10.289	14,727.2	13,534.4	8.813	1.1022	1.1284	2.324
33.4	7947.9	7035.5	12.970	8760.5	7940.6	10.325	9528.4	8754.6	8.839	1.1022	1.1286	2.341
34.4	5142.3	4548.3	13.059	5667.9	5134.8	10.382	6164.8	5662.1	8.880	1.1022	1.1290	2.367
35.4	3327.0	2939.1	13.199	3667.1	3319.5	10.473	3988.6	3661.2	8.943	1.1022	1.1294	2.408
36.4	2152.6	1897.8	13.424	2372.6	2144.9	10.616	2580.6	2366.6	9.044	1.1022	1.1302	2.475
37.4	1392.7	1223.9	13.792	1535.1	1384.8	10.848	1669.6	1528.9	9.206	1.1022	1.3150	2.587
38.4*	901.01	787.5	14.419	993.2	892.8	11.237	1080.2	986.8	9.472	1.1022	1.1338	2.781
39.4	583.0	504.4	15.568	642.6	574.1	11.926	698.2	635.8	9.929	1.1022	1.1381	3.151
40.4	377.2	319.5	18.038	415.7	366.9	13.311	452.2	408.2	10.788	1.1022	1.1482	4.004

* The values listed are the measurement of the elution peak in Fig. 2A.

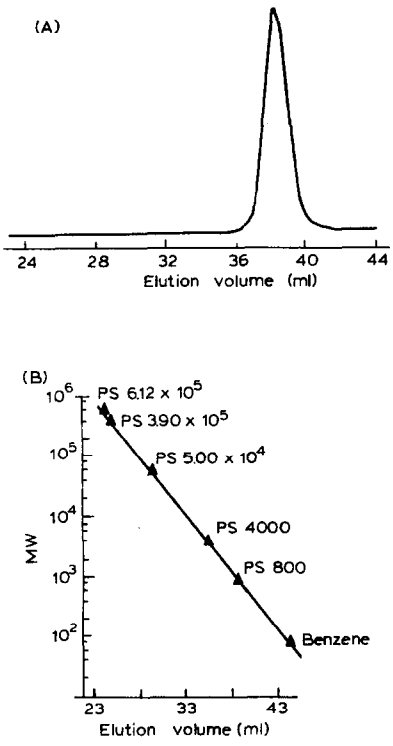

Fig. 2. (A) SEC chromatogram of a polystyrene sample. (B) The plot of log MW *vs.* elution volume of polystyrene standards.

these tables, the values of corrected M_n are close to the nominal values of these standards. The corrected values of polydipersity match the supplied values. The molecular weight deviation percentage of M_n, M_w and M_z decreases as the MW of the standard increases (Tables I, III and IV). The exception of PS 1050 (Table II) probably is due to a larger polydispersity. For the same sample, the percentage deviation decreases in the sequence of M_n, M_w and M_z. This also indicates that the higher-MW portion of the sample is less influenced.

Fig. 2A illustrates a molecular weight calibration curve of polystyrene standards. Fig. 2B shows the SEC chromatogram of a polystyrene sample. The equations of M_n, M_w and M_z of a monochromophore sample are written as

$$M_n = \frac{\Sigma h_i}{\Sigma(h_i/M_i)} \tag{5}$$

$$M_w = \frac{\Sigma h_i M_i}{\Sigma h_i} \tag{6}$$

$$M_z = \frac{\Sigma h_i M_i^2}{\Sigma h_i M_i} \tag{7}$$

where h_i and M_i are the increments of peak height and molecular weight of the chromatogram curve, respectively. As expected, for a sample of polychromophore such as polystyrene, the peak height has to be adjusted in order to represent the actual amount of molecules. Eqn. 8 illustrates the adjusted peak height.

$$h_i' = \frac{h_i}{(M_i - c)/M_0} \tag{8}$$

where c is the combined mass of both end groups of the polymer, and M_0 is the mass of monomer or repeated unit. For an anionically polymerized polystyrene sample, c is the combined mass of a butyl group ($-C_4H_9$) and a hydrogen atom (–H), c = 58, and M_0 = 104 (styrene). Table V lists the uncorrected and corrected values of M_n, M_w and M_z for the polystyrene sample presented in Fig. 2A. In order to understand the correlation of MW deviation with the MW range, we used a HP 85 microcomputer to simulate the calculation. The elution peak in Fig. 2A was used as a model peak. This peak was moving along the elution volume of the linear calibrated MW range. Table V lists a partial portion of the calculated values. The results in Table V are consistent with the HPLC method. The MW deviation decreases as the MW increases, and also in the sequence of M_n, M_w and M_z. The uncorrected polydispersity remains approximately the same over the whole linear calibration range.

In summary, the SEC MW distribution curve obtained with UV detection not only can be used as qualitative comparison of batch to batch varison[6], but also in the determination of MW of regularly repeated polychromophore polymers provided the repeated unit structure and the end groups of the polymer are given.

REFERENCES

1 W. W. Yau, J. J. Kirkland and D. D. Bly, *Modern Size Exclusion Chromatography*, Wiley, New York, 1979, p. 151.
2 M. A. Curtis, J. W. Web, D. C. Warren, V. O. Brandt, F. G. Gerberich, K. B. Raut and L. B. Rogers, *Sep. Sci. Technol.*, 15 (1980) 1413.
3 S.-T. Lai and L. Sangermano, *J. Chromatogr.*, 321 (1985) 325.
4 S.-T. Lai, L. Sangermano and D. C. Locke, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 158.
5 S.-T. Lai, L. Sangermano and D. C. Locke, *J. Chromatogr.*, 312 (1984) 313.
6 W. W. Yau, J. J. Kirkland and D. D. Bly, *Modern Size Exclusion Chromatography*, Wiley, New York, 1979, p. 11.