poor solvation by the mixed solvents for this polymer. Thus, increasing solution temperature results in improved solvation of the polymer chain and expands the conformation. Under these conditions, specific solvation effects are less important in dominating the solution viscosity behavior. At lower ionic contents (~1 mol%) and low alcohol cosolvent levels, the equilibrium described above becomes more dominant in controlling viscosity and its temperature dependence. Under these conditions rather dramatic changes in the apparent molecular weight of the associated polymer chains can arise as a function of temperature, which are atypical of conventional polymer solutions. These results can be interpreted only as a result of interchain associations of the ionic groups.

Clearly, a simple equilibrium describing strictly the ionic associations is not sufficient to describe all the complex ionic interactions but is useful in interpreting the rheology of ionomer solutions.

Conclusion

The insolubility of poly(isoprene-*co*-sodium styrenesulfonate) ionomers in toluene or xylene can be taken as evidence for the presence of ionic association. Solubility behavior of these ionically aggregated elastomers, in common nonpolar solvents of polyisoprene, is similar to that of covalently cross-linked polyisoprene rubber.

Polar cosolvents such as alcohols were believed to preferentially solvate the ionic aggregates, thereby disrupting their association. The extent of ionic association (i.e., degree of physical cross-linking) was shown to be controllable by the amount of polar cosolvents present. This phenomenon can be utilized in practical applications as well as theoretical considerations. For example, polar additives can be applied as processing aids in the fabrication of ionomers, or a controlled degree of cross-linking can be used in verification of various network theories of rubber elasticity.

The solution viscosity of isoprene-based ionomers increased significantly with increasing temperature, providing another potential for these ionomers as viscosity control additives.

Acknowledgment. This work was financed by Exxon Research and Engineering Co.

References and Notes

(1) Canter, N. H. U.S. Patent 3 642 728, 1974.
(2) O'Farrell, C. P.; Serniuk, G. E. U.S. Patent 3 836 511, 1974.
(3) Rahrig, D.; MacKnight, W. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *19* (2), 314.
(4) Siadat, B.; Lundberg, R. D.; Lenz, R. W. *Polym. Eng. Sci.* **1980**, *20* (8), 530.
(5) Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (2), 292.
(6) Siadat, B.; Oster, B.; Lenz, R. W. *J. Appl. Polym. Sci.*, in press.
(7) Neumann, R. M.; MacKnight, W. J.; Lundberg, R. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (2), 298.
(8) Lundberg, R. D. U.S. Patents 3 931 021 (Jan 6, 1976) and 4 118 361 (Oct 3, 1978) (assigned to Exxon Research and Engineering Co.).
(9) Lundberg, R. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (1), 455.
(10) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

Determination of Molecular Weight Distributions of Polyglycol Oligomers by Field Desorption Mass Spectrometry

Robert P. Lattimer*

The BFGoodrich Research and Development Center, Brecksville, Ohio 44141

Gordon E. Hansen

Middle Atlantic Mass Spectrometry Laboratory, The Johns Hopkins University School of Medicine, Baltimore, Maryland 21205. *Received January 22, 1981*

ABSTRACT: Field desorption mass spectrometry (FDMS) has been used to analyze three types of polyglycol oligomers—poly(ethylene glycol), poly(propylene glycol), and poly(tetrahydrofuran). Average molecular weight parameters ($\bar{M}_n$ and $\bar{M}_w$) were determined for several low molecular weight batches of these polymers by using either protonated (MH^+) or cation attachment (MNa^+) ions. Despite the fact that these polymers are thermally and structurally fragile, good agreement was found between the FDMS-derived parameters and those derived via classical methods. With these results it appears that average molecular weight determinations can be made by FDMS for a large number of oligomeric systems.

Introduction

Field desorption mass spectrometry (FDMS) has been shown to be a method of choice for determining molecular weights of nonvolatile and higher molecular weight chemicals.[1,2] Numerous reports from several laboratories have shown that FDMS can be used to obtain good qualitative distributions of oligomers for low molecular weight polymers. Oligomeric mixtures examined in this regard include polyesters,[3] poly(pivalolactone),[4,5] poly(2,2,4-trimethyl-1,2-dihydroquinoline),[6,7] polystyrene,[6-8] poly(propylene glycol),[7-10] poly(ethylene glycol),[10] and oligomeric antioxidants.[3]

We have reported the use of FDMS to determine accurate molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) for a series of low molecular weight polystyrene standards.[11] It was found that FDMS-derived molecular weight parameters compared favorably to values obtained by conventional techniques (vapor pressure osmometry, intrinsic viscosity, kinetic data, and gel permeation chromatography). The polystyrene oligomer molecular weights ranged up to nearly 5300 amu. Polystyrene is a relatively stable polymer in mass spectral analysis and has been used in a number of higher mass studies. Rapid heating of polystyrene has yielded molecular ions up to ~3000 amu (by electron impact or chemical ionization); molecular weight distributions were determined that agreed favorably with standard values.[12] Polystyrene oligomers up to mass ~11 000 have been observed by FDMS.[8] An electrospray ionization

0024-9297/81/2214-0776$01.25/0 © 1981 American Chemical Society

Table I
Molecular Weight Parameters for Polyglycols

polymer	batch	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
PPG[a]	41993	790	≅1.05
PPG	41994	1220	≅1.03
PPG	41985	2020	≅1.02
PEG[b]	1000	1041[c]	
		962[d]	1.05
PEG	1540	1396[c]	
		1365[d]	1.02
PTHF[e]	1050	1050	1.150

[a] Data supplied by Waters Associates. [b] Data from ref 16. [c] End-group titration. [d] Electrohydrodynamic ionization mass spectrometry. [e] Data supplied by Polymer Laboratories.

technique has been used to generate polystyrene ions up to mass ~80 000; the mass analyzer was a low-frequency quadrupole.[13] These studies were all facilitated by the fact that polystyrene is a relatively volatile, nonpolar polymer. Thus, the vaporization/ionization of polystyrene oligomers was reasonably straightforward for a number of different techniques.

More polar, less volatile polymers are generally more troublesome to analyze by mass spectrometry. One general class of polar polymers of commercial importance is the hydroxyl-terminated polyglycols. In order to assess the applicability of FDMS to direct analysis and molecular weight characterization of this general class of polymers, we have studied several commercially available glycol polymers. These include poly(propylene glycol) (PPG, manufactured by Waters Associates), poly(ethylene glycol) (PEG, J. T. Baker), and poly(tetrahydrofuran) (PTHF, Polymer Laboratories).

PPG and PEG yield no molecular ions by normal electron impact (EI) analysis;[14] this is typical of primary alcohols. The EI mass spectra of PEG and PPG are characterized by ions due to water loss and other fragmentation mechanisms. Number-average molecular weights were determined mass spectrometrically (EI) for a number of

Table II
Relative Oligomer Intensities and Molecular Weight Averages for Poly(propylene glycol)

				corr factor		batch 41993		batch 41994		
n	formula	nominal mass[a]	av mass[b]	res 400[c]	res 600[d]	MNa+ [e]	MH+ [f]	MNa+ [e]	MH+ [f]	batch 41985[e]
7	$C_{21}H_{44}O_8$	424	424.6	1.28	1.28	0.14	0.38			
8	$C_{24}H_{50}O_9$	482	482.7	1.33	1.33	0.91	1.32			
9	$C_{27}H_{56}O_{10}$	540	540.7	1.38	1.38	3.32	3.92			
10	$C_{30}H_{62}O_{11}$	598	598.8	1.43	1.43	7.62	7.86	0.02		
11	$C_{33}H_{68}O_{12}$	656	656.9	1.48	1.48	11.6	10.7	0.15		
12	$C_{36}H_{74}O_{13}$	714	715.0	1.53	1.53	14.1	12.5	0.36		
13	$C_{39}H_{80}O_{14}$	772	773.1	1.54	1.58	15.0	12.3	0.75	0.59	
14	$C_{42}H_{86}O_{15}$	830	831.1	1.55	1.64	14.1	11.9	1.85	1.89	
15	$C_{45}H_{92}O_{16}$	888	889.2	1.56	1.70	11.3	10.9	3.10	4.45	
16	$C_{48}H_{98}O_{17}$	946	947.3	1.57	1.76	8.21	9.64	4.84	7.13	
17	$C_{51}H_{104}O_{18}$	1004	1005.4	1.58	1.82	5.50	6.78	6.72	8.81	
18	$C_{54}H_{110}O_{19}$	1062	1063.4	1.59	1.89	3.58	5.03	8.91	10.9	
19	$C_{57}H_{116}O_{20}$	1120	1121.5	1.60	1.93	2.25	3.07	9.64	12.0	
20	$C_{60}H_{122}O_{21}$	1178	1179.6	1.62	1.93	1.31	1.84	10.3	11.4	0.39
21	$C_{63}H_{128}O_{22}$	1236	1237.7	1.63	1.94	0.64	1.06	9.63	10.2	0.71
22	$C_{66}H_{134}O_{23}$	1294	1295.8	1.65	1.95	0.29	0.55	9.84	8.93	0.95
23	$C_{69}H_{140}O_{24}$	1352	1353.8	1.63	1.96	0.13	0.17	8.35	6.50	1.32
24	$C_{72}H_{146}O_{25}$	1410	1411.9	1.60	1.98	0.03	0.06	6.68	5.91	2.20
25	$C_{75}H_{152}O_{26}$	1468	1470.0	1.57	1.99	0.01		5.25	4.66	2.84
26	$C_{78}H_{158}O_{27}$	1526	1528.1	1.55	1.97			4.14	2.94	3.67
27	$C_{81}H_{164}O_{28}$	1584	1586.2	1.52	1.92			3.24	1.47	4.22
28	$C_{84}H_{170}O_{29}$	1642	1644.2	1.51	1.87			2.27	1.26	5.08
29	$C_{87}H_{176}O_{30}$	1700	1702.3	1.49	1.84			1.71	0.67	6.42
30	$C_{90}H_{182}O_{31}$	1758	1760.4	1.48	1.81			1.24	0.29	6.38
31	$C_{93}H_{188}O_{32}$	1816	1818.5	1.47	1.79			0.76	0.13	7.03
32	$C_{96}H_{194}O_{33}$	1874	1876.6	1.46	1.77			0.29		7.08
33	$C_{99}H_{200}O_{34}$	1932	1934.6	1.45	1.76					7.32
34	$C_{102}H_{206}O_{35}$	1990	1992.7	1.44	1.74					6.88
35	$C_{105}H_{212}O_{36}$	2048	2050.8	1.44	1.73					6.72
36	$C_{108}H_{218}O_{37}$	2106	2108.9	1.43	1.73					5.82
37	$C_{111}H_{224}O_{38}$	2164	2167.0	1.43	1.72					5.09
38	$C_{114}H_{230}O_{39}$	2222	2225.0	1.43	1.72					4.40
39	$C_{117}H_{236}O_{40}$	2280	2283.1	1.42	1.71					3.52
40	$C_{120}H_{242}O_{41}$	2338	2341.2	1.42	1.70					2.83
41	$C_{123}H_{248}O_{42}$	2396	2399.3	1.42	1.69					2.31
42	$C_{126}H_{254}O_{43}$	2454	2457.4	1.42	1.69					2.08
43	$C_{129}H_{260}O_{44}$	2512	2515.4	1.42	1.69					1.64
44	$C_{132}H_{266}O_{45}$	2570	2573.5	1.42	1.68					1.28
45	$C_{135}H_{272}O_{46}$	2628	2631.6	1.42	1.68					0.79
46	$C_{138}H_{278}O_{47}$	2686	2689.7	1.42	1.68					0.62
47	$C_{141}H_{284}O_{48}$	2744	2747.8	1.42	1.68					0.27
48	$C_{144}H_{290}O_{49}$	2802	2805.8	1.41	1.69					0.13
					$\overline{M}_n$	805	819	1240	1190	1930
					$\overline{M}_w$	835	855	1280	1220	1980
					$\overline{M}_w/\overline{M}_n$	1.04	1.04	1.03	1.03	1.03

[a] Nominal mass spectrometric molecular weight (C = 12, H = 1, O = 16). [b] Number-average molecular weight for an oligomer isotopic cluster. [c] $M/\Delta M$ = 400 for Varian MAT 311A; see ref 11. [d] $M/\Delta M$ = 600 for Kratos MS-50; see ref 11. [e] Spectra obtained from a methanol solution of the polymer with added NaCl. [f] Spectra obtained from a tetrahydrofuran solution of the polymer (salt free).

Table III
Relative Oligomer Intensities and Molecular Weight Averages for Poly(ethylene glycol)

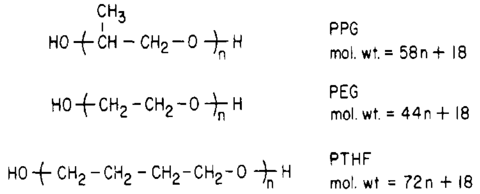
n	formula	nominal mass[a]	av mass[b]	corr factor res = 400[c]	PEG 1000[d]	PEG 1540[d]
8	$C_{16}H_{34}O_{9}$	370	370.4	1.22	0.09	
9	$C_{18}H_{38}O_{10}$	414	414.5	1.25	0.19	
10	$C_{20}H_{42}O_{11}$	458	458.5	1.28	0.31	
11	$C_{22}H_{46}O_{12}$	502	502.6	1.31	0.38	
12	$C_{24}H_{50}O_{13}$	546	546.6	1.34	0.73	
13	$C_{26}H_{54}O_{14}$	590	590.7	1.37	0.77	
14	$C_{28}H_{58}O_{15}$	634	634.7	1.41	0.90	
15	$C_{30}H_{62}O_{16}$	678	678.8	1.44	1.47	
16	$C_{32}H_{66}O_{17}$	722	722.9	1.48	2.06	
17	$C_{34}H_{70}O_{18}$	766	766.9	1.48	4.02	0.12
18	$C_{36}H_{74}O_{19}$	810	811.0	1.49	4.82	0.21
19	$C_{38}H_{78}O_{20}$	854	855.0	1.49	6.66	0.39
20	$C_{40}H_{82}O_{21}$	898	899.1	1.50	8.44	0.85
21	$C_{42}H_{86}O_{22}$	942	943.1	1.50	9.55	1.17
22	$C_{44}H_{90}O_{23}$	986	987.2	1.51	10.0	1.76
23	$C_{46}H_{94}O_{24}$	1030	1031.2	1.52	10.2	2.52
24	$C_{48}H_{98}O_{25}$	1074	1075.3	1.53	9.33	3.52
25	$C_{50}H_{102}O_{26}$	1118	1119.3	1.54	7.85	4.15
26	$C_{52}H_{106}O_{27}$	1162	1163.4	1.55	6.21	5.51
27	$C_{54}H_{110}O_{28}$	1206	1207.4	1.56	4.97	6.60
28	$C_{56}H_{114}O_{29}$	1250	1251.5	1.57	3.71	7.26
29	$C_{58}H_{118}O_{30}$	1294	1295.5	1.58	2.63	8.00
30	$C_{60}H_{122}O_{31}$	1338	1339.6	1.59	1.78	8.58
31	$C_{62}H_{126}O_{32}$	1382	1383.6	1.60	1.26	7.99
32	$C_{64}H_{130}O_{33}$	1426	1427.7	1.60	0.90	7.56
33	$C_{66}H_{134}O_{34}$	1470	1471.8	1.58	0.52	6.63
34	$C_{68}H_{138}O_{35}$	1514	1515.8	1.56	0.24	6.26
35	$C_{70}H_{142}O_{36}$	1558	1559.9	1.54		5.20
36	$C_{72}H_{146}O_{37}$	1602	1603.9	1.52		4.10
37	$C_{74}H_{150}O_{38}$	1646	1648.0	1.51		3.44
38	$C_{76}H_{154}O_{39}$	1690	1692.0	1.49		2.55
39	$C_{78}H_{158}O_{40}$	1734	1736.1	1.48		1.95
40	$C_{80}H_{162}O_{41}$	1778	1780.1	1.47		1.41
41	$C_{82}H_{166}O_{42}$	1822	1824.2	1.46		0.97
42	$C_{84}H_{170}O_{43}$	1866	1868.2	1.45		0.57
43	$C_{86}H_{174}O_{44}$	1910	1912.3	1.45		0.36
44	$C_{88}H_{178}O_{45}$	1954	1956.3	1.44		0.25
45	$C_{90}H_{182}O_{46}$	1998	2000.4	1.43		0.11
				$\bar{M}_n$	1010	1360
				$\bar{M}_w$	1040	1400
				$\bar{M}_w/\bar{M}_n$	1.03	1.03

[a] Nominal mass spectrometric molecular weight (C = 12, H = 1, O = 16). [b] Number-average molecular weight for an oligomer isotopic cluster. [c] $M/\Delta M = 400$ for Varian MAT 311A; see ref 11. [d] MNa^+ ions obtained from a methanol solution of the polymer with added NaCl.

ethylene oxide–propylene oxide copolymers,[14] but the validity of these results has been challenged by other work.[15] Specifically, it is unclear that the complex EI spectra of the oligomers were interpreted correctly in terms of which molecular species were present.[15] FD mass spectra of PPG have recently been studied in detail.[9] Several low molecular weight PPG batches yielded major peaks corresponding to MH^+ ions (or MNa^+ ions if sodium iodide were added to the sample). Strong ions corresponding to fragmentation of the polymer chains were also observed; the mechanisms of fragment ion formation were considered.[9] FD mass spectra of several PPG and PEG samples (including copolymers) have been reported in another recent article.[10] Both MH^+ and MNa^+ ions were observed along with numerous fragment ions. Both of these recent reports[9,10] suggested that the FD mass spectra of polyglycols could be used to estimate molecular weight distributions for the polymers. In neither case, however, were FDMS molecular weight calculations reported.

PEG has recently been analyzed by electrohydrodynamic ionization mass spectrometry (EHMS).[16] The PEG polymers were dissolved in glycerol with NaI added to the solution. EHMS is a soft ionization technique in which polymer solutions are introduced via syringe into the ion source at a high potential vs. a counterelectrode. Sodium attachment ions (MNa^+) were observed by EHMS, and these ions were used to determine $\bar{M}_n$ and $\bar{M}_w$. $\bar{M}_n$ values agreed well with values obtained by end-group titration.[16]

In this report we describe the FDMS analysis of three types of polyglycol oligomers—PPG, PEG, and PTHF:



$$HO\!\left(\overset{CH_3}{\overset{|}{C}H}-CH_2-O\right)_{\!n}H \qquad \text{PPG} \quad \text{mol. wt.} = 58n + 18$$

$$HO\!\left(CH_2-CH_2-O\right)_{\!n}H \qquad \text{PEG} \quad \text{mol. wt.} = 44n + 18$$

$$HO\!\left(CH_2-CH_2-CH_2-CH_2-O\right)_{\!n}H \qquad \text{PTHF} \quad \text{mol. wt} = 72n + 18$$

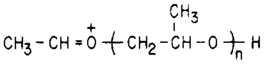
(Although PTHF is not actually prepared from a glycol or an epoxide, its structure is analogous to "normal" polyglycols such as PPG and PEG.) Using either protonated (MH^+) or cation attachment (MNa^+) ions, we have determined average molecular weight parameters ($\bar{M}_n$ and $\bar{M}_w$) for several low molecular weight batches of these polymers. The methods of calculation are essentially identical with those described previously for polystyrene.[11] Despite the fact that these polymers are thermally and structurally fragile, good agreement was found between the

FDMS-derived parameters and those determined by classical methods. It thus appears that FDMS has considerable potential for making average molecular weight determinations for a large number of oligomeric systems.

Experimental Section

Six polyglycol samples were analyzed by FDMS: PEG 1000 and PEG 1540 (J. T. Baker), PPG 41993, 41994, and 41985 (Waters Associates), and PTHF 1050 (Polymer Laboratories). These polymers as received were salt-free. Molecular weight averages determined by methods other than FDMS are given in Table I. All samples except for PPG 41985 were analyzed by using a Varian MAT 311A mass spectrometer (The BFGoodrich Co.) in field desorption mode. Sample PPG 41985 was higher in mass and was analyzed by using a high-field Kratos MS-50 mass spectrometer (The Johns Hopkins University). Instrumental parameters on both instruments were essentially the same as described previously.[11]

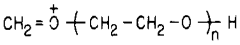
All samples were dissolved in methanol saturated with sodium chloride for analysis. The samples were deposited on field emitters by the normal dipping technique. Standard carbon emitters were used with the MAT 311A, and a silicon emitter was used with the MS-50. (FD mass spectra recorded under similar conditions have been reported previously for PPG[7-10] and PEG.[10]) For PPG the sodium attachment ions (MNa^+) were reasonably strong; proton attachment ions (MH^+) were also present (at relatively lower intensities). The strongest ions, however, were fragment ions (F^+) of probable structure[9]



$$CH_3-CH=\overset{+}{O}\left(CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-O\right)_n H$$

m/z (58n + 45)

For PEG the strongest ions were sodium attachment ions (MNa^+); protonated molecular ions (MH^+) were essentially absent. A series of fragment ions analogous to that observed for PPG was also present to some extent:



$$CH_2=\overset{+}{O}\left(CH_2-CH_2-O\right)_n H$$

m/z (44n + 31)

For PTHF the strongest ions were again the sodium attachment ions (MNa^+). The spectrum was rather complex, however, and several other weaker series of ions were observed, including reasonably intense MH^+ ions.

Mass spectra were also obtained for two of the PPG samples (41993 and 41994) by normal field desorption (without added salt). The samples were dissolved in tetrahydrofuran and deposited on the field emitter (without addition of NaCl). Reasonably intense proton attachment ions (MH^+) were observed, along with numerous intense fragment ions.[9] We were able to make $\bar{M}_n$ and $\bar{M}_w$ calculations for PPG by using either MH^+ (THF solution) or MNa^+ (methanol/NaCl solution) spectra. Intense MH^+ ions were difficult to obtain from THF solutions of PEG and PTHF; hence, molecular weight calculations were made only with MNa^+ ions.

For the molecular weight calculations, spectra obtained by oscillographic trace were used. Six to twelve FDMS runs were made with each polymer sample. Several spectra were recorded (with repetitive scanning, ~12 s per scan) as the field emitter was heated slowly with up to 30-mA heating current. The oligomer peak intensities were summed, and corrections for overlapped isotopic peaks (^{13}C, ^2H, ^{18}O) were applied as described previously.[11] Percent oligomer relative intensities and the FDMS-derived molecular weight parameters ($\bar{M}_n$ and $\bar{M}_w$) are listed in Tables II–IV.

Results and Discussion

The results for the PPG samples will be considered first. For all three samples the FDMS molecular weight parameters (Table II) agreed quite well with values supplied by the manufacturer (Table I). The agreement between $\bar{M}_n$ values was better than 5% in all cases. Note for batches 41993 and 41994 that either protonated molecular ions (MH^+) or sodium attachment ions (MNa^+) could be used with nearly identical results. (The sodium attachment spectra were more intense than the protonated molecular ion spectra, however.)

Table IV
Relative Oligomer Intensities and Molecular Weight Averages for Poly(tetrahydrofuran)

n	formula	nominal mass[a]	av mass[b]	corr factor res = 400[c]	PTHF 1050[d]
5	$C_{20}H_{42}O_6$	378	378.5	1.26	0.29
6	$C_{24}H_{50}O_7$	450	450.6	1.32	0.77
7	$C_{28}H_{58}O_8$	522	522.8	1.39	2.00
8	$C_{32}H_{66}O_9$	594	594.9	1.45	3.11
9	$C_{36}H_{74}O_{10}$	666	667.0	1.52	5.06
10	$C_{40}H_{82}O_{11}$	738	739.1	1.58	6.22
11	$C_{44}H_{90}O_{12}$	810	811.2	1.59	6.59
12	$C_{48}H_{98}O_{13}$	882	883.3	1.60	8.42
13	$C_{52}H_{106}O_{14}$	954	955.4	1.61	8.11
14	$C_{56}H_{114}O_{15}$	1026	1027.5	1.62	8.83
15	$C_{60}H_{122}O_{16}$	1098	1099.6	1.64	8.31
16	$C_{64}H_{130}O_{17}$	1170	1171.7	1.66	7.08
17	$C_{68}H_{138}O_{18}$	1242	1243.8	1.68	6.52
18	$C_{72}H_{146}O_{19}$	1314	1315.9	1.64	5.30
19	$C_{76}H_{154}O_{20}$	1386	1388.0	1.60	4.89
20	$C_{80}H_{162}O_{21}$	1458	1460.1	1.57	4.02
21	$C_{84}H_{170}O_{22}$	1530	1532.2	1.54	3.48
22	$C_{88}H_{178}O_{23}$	1602	1604.3	1.52	2.78
23	$C_{92}H_{186}O_{24}$	1674	1676.5	1.50	2.26
24	$C_{96}H_{194}O_{25}$	1746	1748.6	1.48	1.79
25	$C_{100}H_{202}O_{26}$	1818	1820.7	1.47	1.35
26	$C_{104}H_{210}O_{27}$	1890	1892.8	1.46	0.98
27	$C_{108}H_{218}O_{28}$	1962	1964.9	1.45	0.74
28	$C_{112}H_{226}O_{29}$	2034	2037.0	1.45	0.56
29	$C_{116}H_{234}O_{30}$	2106	2109.1	1.45	0.39
30	$C_{120}H_{242}O_{31}$	2178	2181.2	1.44	0.15
				$\bar{M}_n$	1110
				$\bar{M}_w$	1220
				$\bar{M}_w/\bar{M}_n$	1.10

[a] Nominal mass spectrometric molecular weight (C = 12, H = 1, O = 16). [b] Number-average molecular weight for an oligomer isotopic cluster. [c] $M/\Delta M = 400$ for Varian MAT 311A; see ref 11. [d] MNa^+ ions obtained from a methanol solution of the polymer with added NaCl.

The agreement between FDMS-derived parameters (Table II) and end-group titration/EHMS results[16] (Table I) for the two PEG samples was also quite good. The data indicate that sodium attachment spectra obtained by either FDMS or EHMS[16] give close to the same relative abundances of MNa^+ ions. It should be noted that we also examined two lower molecular weight PEG batches (samples A and B in ref 16) by FDMS. The lower oligomers ($n \lesssim 7$) tended to desorb too rapidly from the field emitter, however, so that accurate relative intensities could not be obtained. The FDMS-derived values for $\bar{M}_n$ and $\bar{M}_w$ were too high as a result. This rapid desorption of lower mass oligomers was noted previously in the case of polystyrene;[11] this effect limits the FDMS determination of molecular weight averages for certain polymer batches (depending on volatility).

The FDMS-derived molecular weight averages for PTHF (Table III) were found to agree well with the data sheet values (Table I). $\bar{M}_n$ determined by FDMS is ~6% higher than $\bar{M}_n$ determined by the manufacturer. The agreement is satisfactory but may indicate that the lower mass oligomers are somewhat too volatile for optimal determination of their relative intensities.

In summary, we have shown that FDMS can be used to determine accurate molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$)

for a series of polar glycol polymers. This is true despite the fact that these polymers are not considered "good desorbers" under field desorption analysis. The polymers tended to give reasonably strong fragmentation in the FD mode, yet we found that MH$^+$ and/or MNa$^+$ ions could be used to give good molecular weight averages. The utility of sodium cation attachment was demonstrated for PEG, PPG, and PTHF. This is an established technique in FD; several reports describing this and related methods have appeared in the literature over the past few years.[2] Indeed MNa$^+$ mass spectra were reported for PEG and PPG in previous studies.[8-10]

The utility of field desorption mass spectrometry for determining molecular weight distributions of oligomeric mixtures has now been demonstrated for a number of polymers. In addition to PEG, PPG, and PTHF, average molecular weight parameters have been determined by FDMS for polystyrene[11] and a bisphenol A-epichlorohydrin copolymer.[17] It thus appears that FDMS has considerable potential for $\bar{M}_n$ and $\bar{M}_w$ determinations for a large number of oligomeric systems.

Acknowledgment. Appreciation is expressed to The BFGoodrich Co. and to the National Science Foundation (Middle Atlantic Mass Spectrometry Laboratory) for support of this work. The support and encouragement of J. B. Pausch (The BFGoodrich Co.) and C. C. Fenselau and R. J. Cotter (The Johns Hopkins University) are acknowledged. R. E. Harris (The BFGoodrich Co.) assisted with some aspects of the mass spectrometry. Helpful discussions with D. J. Harmon (The BFGoodrich Co.) and K. D. Cook (University of Illinois) are also appreciated.

Note Added in Proof. By lowering the ion source temperature to ~100 °C, we were able to obtain good molecular weight averages for two lower mass PEG batches (samples A and B in ref 16).

References and Notes

(1) Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectrometry"; Pergamon Press: New York, 1977.
(2) Schulten, H.-R. *Intl. J. Mass Spectrom. Ion Phys.* **1979**, *32*, 97.
(3) Lattimer, R. P.; Welch, K. R. *Rubber Chem. Technol.* **1980**, *53*, 151.
(4) Wiley, R. H.; Cook, J. C., Jr. *J. Macromol. Sci., Chem.* **1976**, *A10*, 811.
(5) Wiley, R. H. *Macromol. Rev.* **1979**, *14*, 379.
(6) Lattimer, R. P.; Harmon, D. J.; Welch, K. R. *Anal. Chem.* **1979**, *51*, 1293.
(7) Lattimer, R. P.; Welch, K. R.; Pausch, J. B.; Rapp, U. Varian MAT 311A Application Note No. 27, 1978.
(8) Matsuo, T.; Matsuda, H.; Katakuse, I. *Anal. Chem.* **1979**, *51*, 1329.
(9) Neumann, G. M.; Cullis, P. G.; Derrick, P. J. *Z. Naturforsch.* **1980**, *35A*, 1090.
(10) Saito, J.; Toda, S.; Tanaka, S. *Shitsuryo Bunseki* **1980**, *28*, 175.
(11) Lattimer, R. P.; Harmon, D. J.; Hansen, G. E. *Anal. Chem.* **1980**, *52*, 1808.
(12) Udseth, H. R.; Friedman, L. *Anal. Chem.* **1981**, *53*, 29.
(13) Friedman, L. 28th Annual Conference on Mass Spectrometry and Allied Topics, New York, May 25-30, 1980, Workshop on High Mass Measurements.
(14) Lee, A. K.; Sedgwick, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 685.
(15) Weibull, B. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1633.
(16) Lai, S.-T. F.; Chan, K. W.; Cook, K. D. *Macromolecules* **1980**, *13*, 953.
(17) Saito, J.; Toda, S.; Tanaka, S. *Bunseki Kagaku* **1980**, *29*, 462.