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phase formation can be rationalized by treating the system of entangled, stressed chains under flow as equivalent to a thermodynamic model system consiting of chains with a reduced flexibility. In such a case, one finds that a liquid–liquid phase separation always occurs in a fashion such that chains in the more concentrated phase have a lower flexibility than those in the dilute phase. For the UHMWPP and UHMWPEO systems, the inherent chain stiffness factors are 1.61 and 1.38, respectively, which correlates with our observation of well-defined precursor formation in PP over a wide range of temperatures 83–120 °C) well in excess of the normal, quiescent crystallization temperature (~72 °C) while UHMWPEO precursors were only found over a narrow range 35–36 °C) near the PEO quiescent crystallization temperature (~31 °C). Likewise since the PP precursors are stable at small undercoolings, they have measurable lifetimes before the crystalline transformation occurs as opposed to the PEO precursors, which, since their effective undercooling is larger, transform almost immediately. On the basis of the poor integrity of the PEO fibers and observations from earlier DSC studies[20] one also expects little or no extended-chain crystals to be present in the fibers that do form. These results are also consistent with the strong tendency for stirring-induced network formation and subsequent phase separation we observed with the PP as opposed to the much greater tendency of the stirred PEO solutions to form crystal aggregates on cooling.

Clearly, molecular weight and concentration also play an important role in the precursor formation–crystallization process as noted by the fact that fibers did not form from 1 wt % LMWPP solutions above 105 °C nor from 0.1% solutions under any conditions. Furthermore, though crystallization could be observed below 94 °C in the former case, the relative weakness of the precursor formation and lack of extended-chain crystal formation was apparent in the poor integrity of the fibers that were ultimately produced. Increasing the polymer concentration should lead to more effective entanglement and precursor formation; however, with our present apparatus flow experiments above 1 wt % were not possible due to the increased viscosity. Fortunately, the 1 wt % LMWPP solutions formed enough chain entanglements, without a dramatic increase in viscosity, so that the precursor formation mechanism could be directly observed.

Summary

By way of brief summary, these studies along with our earlier reports clearly substantiate that precursor formation followed by crystal growth is the fundamental process by which flow-induced crystallization occurs. The present studies also indicate the important role of polymer molecular weight and chain stiffness (whether inherent or induced by entanglement formation) in affecting both the rate and quality of the fibrillar precursor formation and subsequent oriented crystallization.

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References and Notes

(1) Rietveld, J.; McHugh, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1513.
(2) Pennings, A. J. *Proc. Int. Symp. Fiber Sci. Technol.*, Hakone, Japan, 1985; p 20.
(3) Rietveld, J.; McHugh, A. J. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 919.
(4) Rietveld, J.; McHugh, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2339.
(5) McHugh, A. J.; Rietveld, J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2359.
(6) Vrahopoulou-Gilbert, E.; McHugh, A. J. *Macromolecules* **1984**, *17*, 2657.
(7) Vrahopoulou, E. P.; McHugh, A. J. *J. Appl. Polym. Sci.* **1986**, *31*, 399.
(8) Andruszka, K. W., personal communication.
(9) Vrahopoulou, E. P. Ph.D. Thesis, University of Illinois, Urbana, 1986.
(10) Graessley, W. W. *J. Chem. Phys.* **1965**, *43*, 15.
(11) Pelzbauer, Z.; Manley, R. St. John *J. Macromol. Sci., Phys.* **1970**, *B4*, 761.
(12) Blunk, R. H. M.S. Thesis, University of Illinois, Urbana, 1985.
(13) Pennings, A. J. *J. Polym. Sci., Part C* **1967**, *16*, 1799.
(14) McHugh, A. J. *Polym. Eng. Sci.* **1982**, *22*, 15.
(15) McHugh, A. J.; Ejike, E.; Silebi, C. A. *Polym. Eng. Sci.* **1979**,*19*, 414.
(16) Samuels, R. J. *Structured Polymer Properties*; Wiley: New York, 1974; Chapter 2.
(17) Shah, J. K.; Lahti, L. E. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 304.
(18) Wikjord, A. G.; Manley, R. St. John *J. Macromol. Sci., Phys.* **1970**, *B4*, 397.
(19) Flanagan, R. D.; Rijke, A. M. *J. Polym. Sci., Part A-2* **1972**, *10*, 1207.
(20) Rijke, A. M.; McCoy, S. *J. Polym. Sci.* **1972**, *10*, 1845.

Laser Desorption–Fourier Transform Mass Spectrometry for the Characterization of Polymers

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ABSTRACT: Laser desorption–Fourier transform mass spectrometry has been applied to a variety of polymers with average molecular weights of up to 6000. Spectra obtained are dominated by peaks corresponding to the K^+ or Na^+ attachment to the various oligomers, making molecular weight characterization simple. Calculated molecular weights for the polymers examined are in good agreement both with nominal values supplied by the manufacturers and with end-group titration values. No mass discrimination is observed in either the ionization mechanism or mass spectrometer up to masses of ~7000 amu, and no significant fragmentation is observed in the polymers studied.

The molecular weight distribution (MWD) of a polymer is an important factor in determining the suitability of a given polymer for a particular application. Other important parameters include chemical composition, stereochemistry, topology, and morphology. A variety of analytical techniques have been developed for characterizing the molecular weights of polymers. These can be divided into methods that provide average values of molecular weight and those that provide the full MWD. These can be subdivided further into absolute and relative methods,

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depending upon whether standards are required. The most commonly used are averaging methods, which determine number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$). The mathematical relationship for $\bar{M}_n$ and $\bar{M}_w$ is given in eq 1 and 2, where N_i is the number

$$\bar{M}_n = \sum N_i M_i / \sum N_i \tag{1}$$

$$\bar{M}_w = \sum N_i M_i^2 / \sum N_i M_i \tag{2}$$

of moles of molecules of molecular weight M_i in the polymer. Absolute methods for $\bar{M}_n$ determination include end-group titration, osmometry, ebulliometry, and cryoscopy, while light scattering provides $\bar{M}_w$ values. Although these methods provide important information on polymers, being averaging methods, they neither provide the MWD of a polymer nor data on oligomer composition, degree of branching, or purity.

The most common technique for measuring molecular weight averages and molecular weight distribution is size exclusion chromatography (SEC). Because SEC is a relative method, it requires well-characterized molecular weight standards of narrow distribution and similar chemical composition and topology in order to prevent shifting of the molecular weight calibration. Attempts at achieving universal calibration for SEC[1] have had good results for certain polymers as has the use of on-line low-angle laser light scattering detection,[2] from which the MWD can be determined. The latter method requires prior knowledge of the specific refractive index increment, $d\eta/dc$ (η is refractive index and c is concentration), and use of a concentration-sensitive detector. However, in practice, SEC often is employed to determine whether a MWD has been altered and not for determination of absolute values.

An absolute method for determining the molecular mass of each oligomer is clearly preferable to the more classical methods of polymer analysis. Mass spectrometry offers such a method for the determination of absolute MWD and, in addition, can provide data on molecular composition, degree of branching, end-group numbers, and polymer purity.

The major limiting factors in analysis of lower molecular weight polymers (MW = 1000–10 000) by mass spectrometry include the low volatility and thermal lability of such polymers as well as the effective mass range of the mass spectrometers used. Pyrolysis mass spectrometry has been used to circumvent these problems.[3-5] With the development of "soft" ionization techniques such as field desorption (FD),[6-11] plasma desorption (PD),[12] fast-atom bombardment (FAB),[13,14] electrohydrodynamic ionization (EH),[15,16] and secondary ion mass spectrometry (SIMS),[17,18] mass spectrometry has begun to realize some of its potential for polymer analysis. Several recent detailed reviews have surveyed the status[19,20,24] of applications of mass spectrometry for polymer analysis.

Even with the development of "soft" ionization techniques, mass discrimination can still be a considerable problem due to the transmission/detection limitations of mass spectrometers, excessive fragmentation, or discrimination of the ionizing method employed. Recently, laser desorption–mass spectrometry has emerged as an alternative "soft" ionization technique. Analysis of some polyglycol polymers using a time of flight (TOF) mass spectrometer and a laser desorption source has recently been reported,[21] as have TOF–SIMS analyses of nylons.[22] Good molecular weight distributions for the low molecular weight polyglycol polymers were obtained. Although TOF mass spectrometers have impressive mass ranges, they possess limited resolution. In addition, although the analyzer itself does not show mass discrimination, electron multiplier detection still produces mass discrimination when operated in the linear mode. Postacceleration of the ions can reduce this effect[21] although not eliminate it.

Fourier transform mass spectrometry (FTMS) offers several unique advantages as a high-mass analyzer. As with TOF mass spectrometers, the lack of focusing optics provides a wide mass range without mass discrimination. The use of ion-image current detection in FTMS, with its theoretical lack of mass discrimination, alleviates the problem of mass-dependent response typically encountered with electron multiplier detection. In addition, FTMS is a high-resolution technique. The principles of FTMS have been reviewed in detail elsewhere.[23] A laser desorption (LD) source coupled with FTMS has been demonstrated[24] and a survey of potential applications, including oligopeptides and polymers, published.[25] Laser desorption FTMS also has been employed to characterize poly(*p*-phenylenes) synthesized in a variety of ways.[26] Here, application of LD–FTMS to the analysis of selected polymers in the 1000–10 000 molecular weight range is described. These results are compared with previous mass spectrometric methods, as appropriate.

Experimental Section

All mass spectra were obtained with a Nicolet 1000 Fourier transform mass spectrometer equipped with a 3.0 T superconducting magnet and a laser desorption interface that has been described previously.[24] The Tachisto 215G pulsed CO_2 laser's grating has been replaced with a reflector that passes all CO_2 laser wavelengths.

Sample Preparation. All polymers were obtained from commercial sources and used as received. Polystyrene 2000 was obtained from Pressure Chemical Co., poly(ethylene glycol) (PEG) 6000 from Merck, poly(ethylene glycol methyl ether) (PEGME) 5000 from Aldrich, and poly(ethylenimine) (PEI) 600 and 1200 and poly(caprolactone diol) 2000 from Polysciences. The remaining PEG's, (600, 1000, 1450, and 3350) and poly(propylene glycol) (PPG) 4000 were obtained from Sigma. Samples, normally ~1 mg, were dissolved in ~200 μL of methanol (except polystyrene, which was dissolved in $CHCl_3$). Solutions were then doped with ~1 mg of KBr (except PEGME 5000, which was doped with NaCl) and transferred to a circular stainless steel probe tip that was attached to a standard direct insertion probe. Mass spectra were acquired in the broad-band mode with a high-frequency cutoff of 300 KHz, (corresponding to a lower mass limit of ~150 amu). For molecular weight distribution determinations, a minimum of 5 spectra were averaged in the time domain. After each laser pulse, corresponding to the acquisition of a single mass spectrum, the probe was rotated to expose a fresh surface for the next laser pulse. Although the reproducibility of the spectra were generally quite good for the polymers studied, small changes in the relative intensities (a few percent, at most) of individual oligomers were sometimes observed, necessitating averaging spectra to ensure good signal-to-noise ratio and accurate molecular weight distributions. Laser spot sizes were on the order of 1 mm in diameter, which, when a 1.2-cm diameter probe tip was used, allowed a large number of spectra to be collected for a single sample. Normally, 64K transient data were collected, stored to disk, subsequently base line corrected, sine-bell apodized, and magnitude mode Fourier transformed. Samples were allowed to pump down to ~1×10^{-8} torr or less after insertion into the vacuum system (typically 30–60 min) prior to analysis. Similarly, delays of 3–5 s before ion detection were employed after the laser pulse to reduce the pressure of neutrals in the analysis cell.

Results and Discussion

Polymer Spectra. LD–FTMS positive ion spectra of the polymers in the present study are characterized by abundant ions corresponding to cation (Na^+ or K^+) attachment to the individual oligomers and very little fragmentation. This is particularly important for calculating molecular weight distributions. Undoped spectra produced

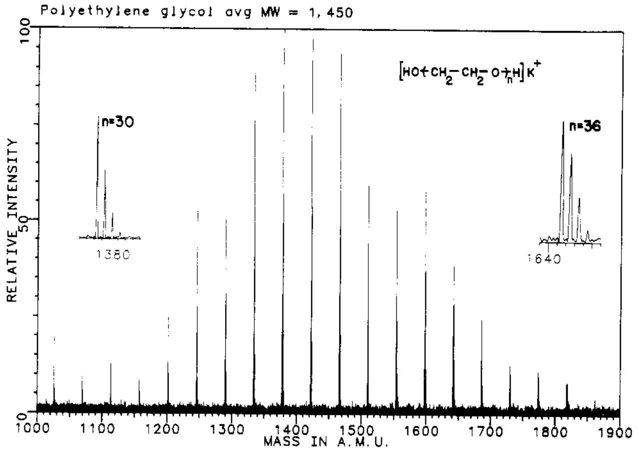

Figure 1. LD-FTMS spectrum of PEG 1450 doped with KBr.

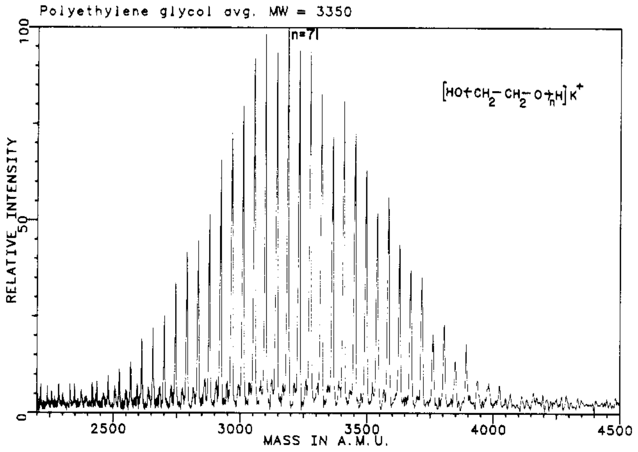

Figure 2. LD-FTMS spectrum of PEG 3350 doped with KBr.

both $(M + Na)^+$ and $(M + K)^+$, presumably from adventitious salts introduced either during sample synthesis or subsequent sample preparation. Although this can be useful in spectral interpretation, as fragments often do not exhibit cation attachment, it complicates the spectrum and molecular weight distribution calculations. Addition of a suitable salt dopant, normally NaCl or KBr, normally results in exclusively Na^+ or K^+ attachment, respectively. Under the present experimental conditions, no multiply charged ions are observed. A series of 5 different poly(ethylene glycols) (PEG) with average molecular weights between 600 and 6000 have been examined. Representative spectra demonstrating typical resolution obtained and the method's ability to produce and detect ions in excess of 7000 amu are shown in Figures 1–3 (PEG 1450, 3350, and 6000). Decreased resolution at higher masses is caused by two factors. Resolution in FTMS (full width at half-height definition) is described by eq 3 where q/m is the

$$m/\Delta m = qB\tau/2m \qquad (3)$$

charge to mass ratio, B is the magnetic field strength, and τ is the time constant for signal decay. As can be seen, resolution is inversely proportional to mass. Also, the frequency of the observed signal decreases as the mass is increased, as can be seen in eq 4.

$$\omega = qB/m \qquad (4)$$

At mass 6000, the observed frequency is approximately 7.5 kHz. The present instrumentation is one of the first commercial systems produced and was not originally designed for masses greater than 3000. Although modifications have been made to the electronics, allowing higher masses to be detected, there is more noise in this frequency range than at higher frequencies. Thus, the length of time during which signal can be observed is diminished, resulting in somewhat lower resolution at higher masses. Current designs of newer instruments have addressed this problem. It should be noted that increasing the magnetic field strength would improve the resolution (eq 3) while reducing the noise problem by shifting the signal for a given mass to higher frequency. Because unit mass resolution can be obtained to at least m/z 2000 with the present instrument and LD source, an 8-T magnet would increase the unit resolution mass limit to almost 6000 amu for singly charged ions.

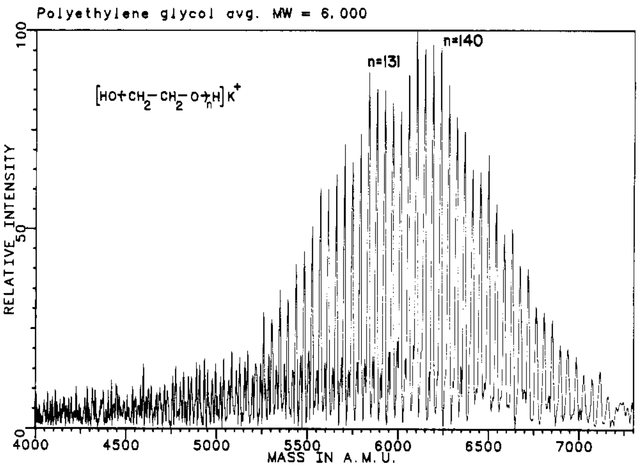

Figure 3. LD-FTMS spectrum of PEG 6000 doped with KBr.

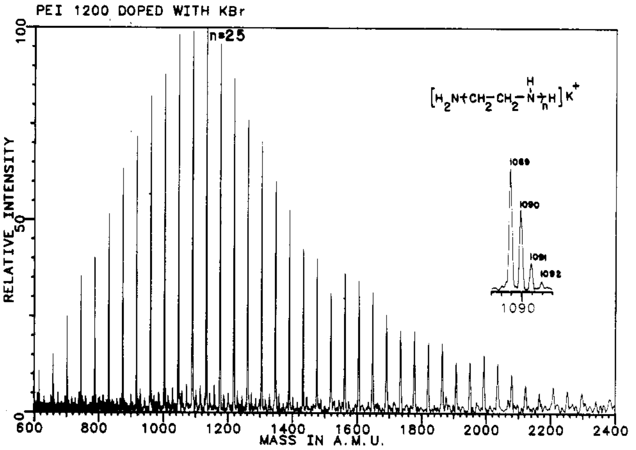

Figure 4. LD-FTMS spectrum of PEI 1200 doped with KBr.

No significant fragmentation is observed for the lower molecular weight poly(ethylene glycols); however, PEG 3350 and PEG 6000 show small secondary envelopes corresponding to dehydration. This water loss was not found for either PEGME 5000 or PPG 4000, suggesting it may be unique to the higher mass PEG's. Although PEGME 5000 was similar to the PEGs with respect to the types of ions produced (with the exception of Na attachment due to the use of NaCl as the dopant), the ions were generally of lower total abundance than PEG's of similar mass. This may be due to its terminal methyl group. PPG 4000, however, was much more susceptible to fragmentation if excess laser power was used. When a low enough laser power was used, its mass spectrum was free of significant fragmentation, although total ion abundances were more similar to those of PEGME than to PEG.

In addition to PEG, several other polymers have been examined. PEI 1200 (Figure 4) is similar to the PEG's, both in structure and spectral characteristics. Cation attachments to individual oligomers are again the only

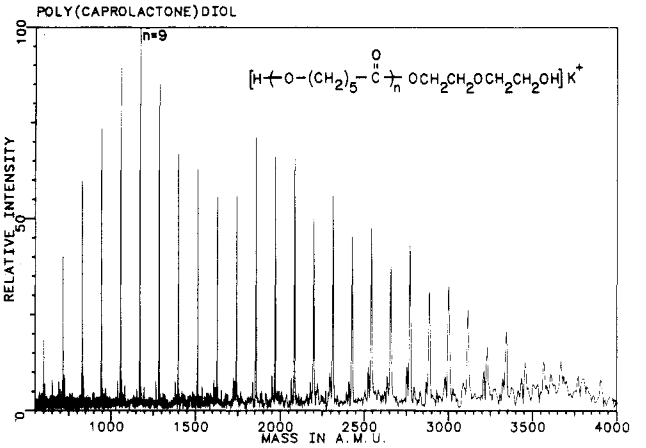

Figure 5. LD–FTMS spectrum of poly(caprolactone diol) 2000 doped with KBr.

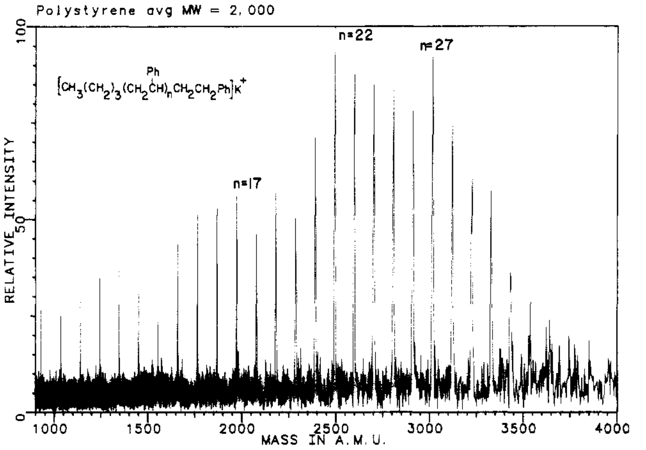

Figure 6. LD–FTMS spectrum of polystyrene 2000 doped with KBr.

significant ions observed. The polymer resulting from ring-opening polymerization of ethylene imine contains primary, secondary, and tertiary amine groups and can be highly branched. PEI can also be produced in an unbranched form by the isomerization polymerization of unsubstituted 2-oxazolines. Very minor peaks arising either from fragmentation or impurities are also evident in the spectrum. Also observed is a series (17 amu lower) corresponding to loss of NH_3, analogous to the H_2O loss observed for higher mass PEG's.

The polyester, poly(caprolactone diol) 2000, has also been examined by LD–FTMS. As in the previous polymers, the spectrum (Figure 5) is dominated by K^+ attachment to the oligomers. Even though a 114-amu repeating unit is evident, the end group corresponds to a mass of 106 amu, which is not consistent with any simple fragmentation pathway. Previous mass spectral investigation of this polymer by FD noted the same results and suggested that the terminal group might be a diethylene glycol used in molecular weight control.[27] We have adopted this assignment as the most plausible. Again, as in the PEG's, a small amount of dehydration occurs.

A nonpolar polymer, polystyrene 2000, was also examined. Again, perhaps surprisingly considering its nonpolar nature, K^+ attachment to the oligomers is observed (Figure 6) and there is no significant fragmentation.

Molecular Weight Distributions. In order to obtain accurate molecular weight distributions of polymers by mass spectrometry, both ion production and ion sampling must be nonbiased. It has already been mentioned that FTMS does not suffer from mass discrimination, either in ion separation or detection, unlike most other forms of mass spectrometry. However, this still leaves open the possibility of mass discrimination due to the laser ionization process. To answer this question, commercial polymers that are reasonably well-characterized by more classical methods have been chosen for characterization of MWD by LD–FTMS.

Table I
Polymer Number- and Weight-Average Molecular Weights Determined by LD-FTMS

polymer	$\bar{M}_n{}^a$	$\bar{M}_w{}^b$	$\bar{M}_w/\bar{M}_n{}^c$	end group[d] $\bar{M}_n$	$\bar{X}_n{}^e$	$\bar{X}_w{}^f$
PEG 600	661	684	1.03		14.6	15.1
PEG 1000	1088	1115	1.03		24.3	24.9
PEG 1450	1384	1404	1.01	1349	31.1	31.5
PEG 3350	3160	3189	1.01	3297	71.4	72.1
PEG 6000	6033	6061	1.01		136.7	137.3
PPG 4000	5518	5563	1.01	4757	94.8	95.6
PEI 600	685	742	1.08		15.5	16.8
PEI 1200	1137	1226	1.08		26.0	28.1
polystyrene 2000	2375	2560	1.08		21.3	23.1
poly(caprolactone-diol) 2000	1776	2086	1.17	1973	14.6	17.4
PEGME 5000	5694	5721	1.01		128.7	129.3

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Measure of polydispersity. [d] Determined by end-group titration. [e] Number-average degree of polymerization. [f] Weight-average degree of polymerization.

Several points must be considered when using a mass spectrum for determining a polymer's MWD. Even if one assumes the spectrum is representative of the individual oligomers, the constributions from minor stable isotopes (i.e., isotopes other than ^{12}C, ^{1}H, ^{14}N, ^{16}O, etc.) must be taken into account, especially as the mass increases. The resolution in FTMS changes with mass (decreasing as mass increases). Both problems are circumvented in the present study by integrating the area for all isotopes for a given oligomer and using the molecular weight of the corresponding monoisotopic formula while also correcting for cation attachment to the observed masses. No attempt was made to correct for any of the small amount of fragment ions, as these were considered to be insignificant. Figure 7 graphically depicts the results of the integration for PEI, poly(caprolactone diol), polystyrene, and PEGME. As expected, the integrals closely follow the mass spectral distribution. These data can be used to calculate $\bar{M}_n$ and $\bar{M}_w$ from eq 1 and 2 as well as the polydispersity ($\bar{M}_w/\bar{M}_n$) and average oligomer length ($\bar{X}_n$ and $\bar{X}_w$) for each average molecular weight. The results are summarized in Table I. A unique feature of FTMS for the calculation of MWD is the variable resolution that can be obtained from a single experiment. Since resolution is directly related to the observation time of the signal (assuming incomplete dampening), the signal can be observed until completely damped (assuming adequate computer memory) and stored to disk. Maximum resolution, which is important for structural characterization, can be obtained by Fourier transformation of all data points acquired, at the expense of decreased signal to noise ratio (S/N). Alternately, for MWD calculations, a lower number of points may be transformed, improving S/N and enhancing the ability to observe low-abundance oligomers at the expense of resolution. Most spectra presented in this paper have been processed at lower resolution for clarity. The spectrum of PEI 1200 (Figure 4) is a good example. Here, a higher resolution inset produced by Fourier transformation of more data points is included. It should be stressed that the maximum obtainable resolution is still dependent on the time required for signal damping. However, variable

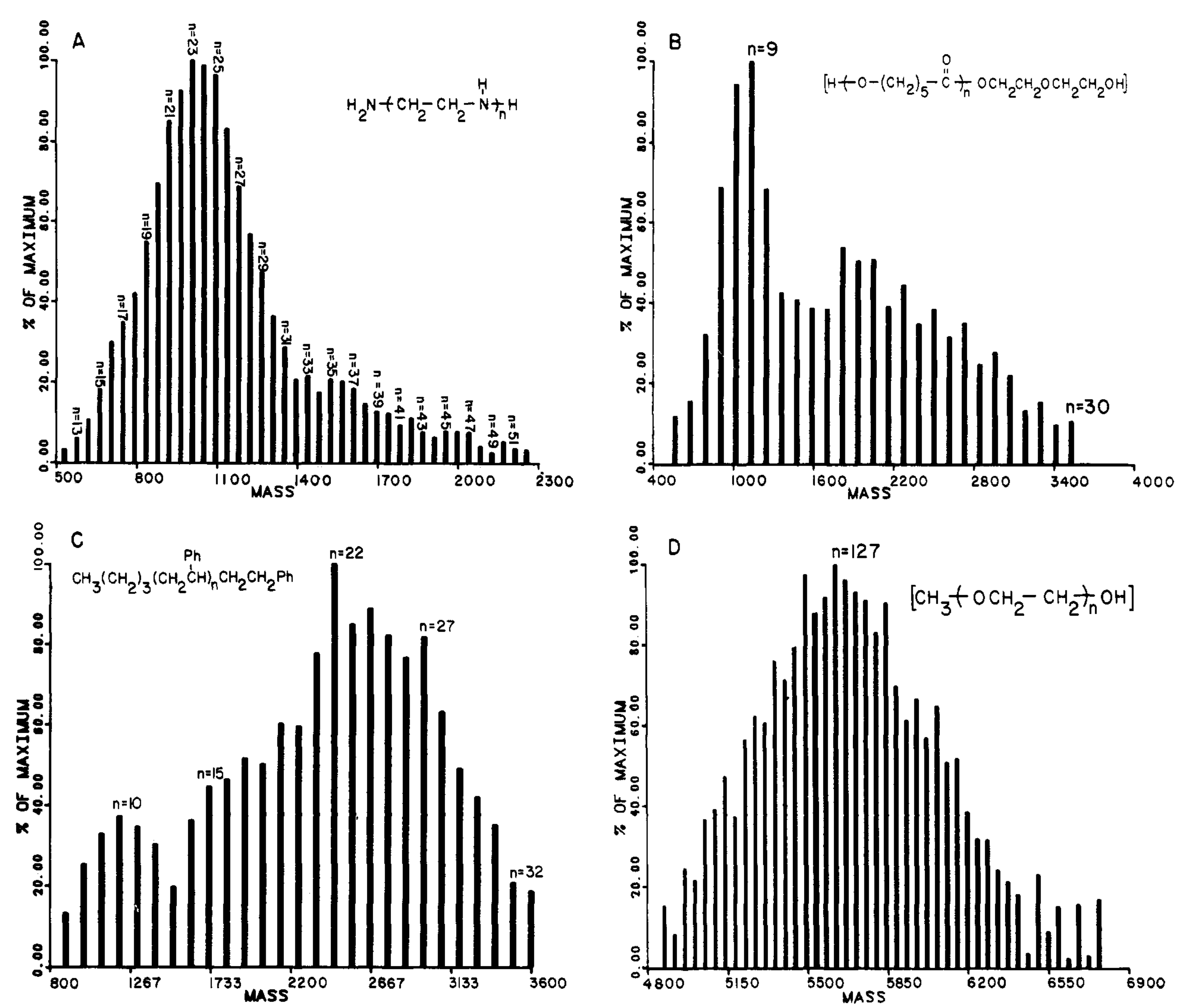

Figure 7. Molecular weight distributions calculated from integrated intensity values for (a) PEI 1200; (b) poly(caprolactone diol) 2000; (c) polystyrene 2000; (d) PEGME 5000.

resolution is useful for enhancing weaker peaks, thus improving the MWD calculations.

The average molecular weights in Table I are in good agreement with the nominal molecular weight designations of the manufacturers. Additional data for the polystyrene sample from the manufacturer included values of $\bar{M}_v$ = 2111 (intrinsic viscosity), $\bar{M}_w$ = 1790 (light scattering), $\bar{M}_n$ = 1790 (vapor phase osmometry), and $\bar{M}_{nk}$ = 2000 based upon the stoichiometry of the polymerization reaction. In addition, an $\bar{M}_w/\bar{M}_n$ value of 1.06 was reported. The latter is in reasonably good agreement with the mass spectrometrically determined value of 1.08. However, either the $\bar{M}_w$ or $\bar{M}_n$ value reported must be in error as they cannot be equal with a $\bar{M}_w/\bar{M}_n$ = 1.06. This, coupled with the fact that $\bar{M}_v$ theoretically should fall between $\bar{M}_n$ and $\bar{M}_w$ (i.e., $\bar{M}_n \leq \bar{M}_v \leq \bar{M}_w$) for polydisperse polymers puts all of the manufacturer-reported values in doubt. Similar inconsistencies have been noted in the past[7] for low molecular weight polystyrene from the same source.

End-group titration is a common method used in determining number-average molecular weight for nonbranched polymers that have known numbers of end groups. Hydroxyl-terminated polymers can be esterified with phthalic anhydride under reflux conditions and the excess reagent titrated with base to yield an average hydroxyl content as described in ASTM standard method D4274-83.[28] Although this method is susceptible to a variety of interferences, it has been shown to work well for lower molecular weight poly(ethylene glycols).[16] The results of such determinations for PEG 1450, PEG 3350, PPG 4000, and poly(caprolactone diol) 2000 are also presented in Table I. The PEG values are within a few percent of the mass spectrometrically determined values while the PPG value falls between the manufacturer's nominal average weight and the mass spectrometrically determined $\bar{M}_n$. It should be noted that the PPG did not give as sharp an end point as the other samples. Overall, the average molecular weights determined from end-group titration are in close agreement with the mass spectrometrically determined $\bar{M}_n$. Many of the remaining hydroxyl-terminated polymers could not be analyzed by this method due to the large amount of sample required in this procedure (7–30 g).

A variety of polyglycols have been characterized by mass spectrometric means, including EHD-MS,[16] FD-MS,[11] FAB-MS,[13] LD-TOP-MS,[21] and TOF-SIMS.[22] A comparison of the results obtained by these techniques for low molecular weight PEG's ($\bar{M}_n$ = 400–1400) is presented by Mattern and Hercules,[21] which suggests that FD-MS produces the most consistent results. The present results for similar molecular weight PEG's by LD–FTMS compare favorably with these previous determinations. In addition, LD–FTMS has been shown to produce good MWD data to at least mass 6000. Similarly, poly(ethylenimine) has also been studied by FD-MS,[29] FAB-MS,[29] and EH-MS[30] in addition to LD–FTMS. Unlike the poly(ethylene gly-

Table II
Comparison of Mass Spectrometric Analyses of Poly(ethylenimines)

sample	instrument	method	$\bar{M}_n$[a]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[c]
PEI 600	MAT 311A[d]	FD	553	583	1.05
PEI 600	MAT 731[d]	FD	557	627	1.13
PEI 600	MAT 311A[d]	FAB	513	585	1.14
PEI 600	MS-9[e]	EH	399		
PEI 600	FTMS-1000[f]	LD	685	742	1.08
PEI 1200	MAT 311A[d]	FD	739	850	1.15
PEI 1200	MAT 731[d]	FD	766	860	1.12
PEI 1200	MAT 311A[d]	FAB	551	636	1.15
PEI 1200	MS9[e]	EH	505		
PEI 1200	FTMS-1000[f]	LD	1137	1226	1.08

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Measure of polydispersity. [d] From ref 27. [e] From ref 28. [f] This study.

cols), FD-MS, FAB-MS, and EH-MS all gave substantially lower $\bar{M}_n$ results than the nominal molecular weight provided by the manufacturer (Table II). LD-FTMS, however, does provide values consistent with the nominal molecular weight. Because the samples are frm the same manufacturer and lot, gross sample differences can be ruled out. Several explanations for the low values have been proposed, including excessive fragmentation for FAB-MS and sampling bias in EH-MS. Excessive mass discrimination by the mass spectrometers employed can be ruled out based upon the PEG results.

Conclusions

LD-FTMS has been shown to provide an accurate method for the characterization of polymer molecular weight averages and distributions. Minor instrumental modifications should improve not only the upper mass range limit but also the mass spectral resolution and sensitivity. This, coupled with the information available from mass spectrometry for the analysis of structural features of both new and existing polymers, as well as identification of low-level impurities, should make LD-FTMS a powerful polymer characterization tool. Although a limited number of nonpolar polymers (e.g., polystyrene) have been examined to date, it is obviously necessary to investigate a broader range in order to delineate the general polymer analysis capability of LD-FTMS. Also, the study of more complex copolymers (alternating, random, and block) to determine how much detailed structural information will be available by LD-FTMS should be pursued.

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References and Notes

(1) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753–759.
(2) Ouano, A. C. *J. Chromatogr.* **1976**, *118*, 303–312.
(3) Maeuzelarr, H. L. C.; Kistemaker, P. G.; Posthumus, M. A. *Biomed. Mass. Spectrom.* **1974**, *1*, 312.
(4) Adams, R. E. *Anal. Chem.* **1983**, *55*, 414–416.
(5) Gardella, J. A.; Graham, S. W.; Hercules, D. M. *Adv. Chem. Ser.* **1983**, *No. 203*, 635–676.
(6) Lattimer, R. P.; Schulten, H. R. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 105–116.
(7) Lattimer, R. P.; Harmon, D. J.; Hansen, G. E. *Anal. Chem.* **1980**, *52*, 1808–1811.
(8) Matsuo, T.; Marsuda, H.; Katakuse, I. *Anal. Chem.* **1979**, *51*, 1329–1331.
(9) Lattimer, R. P.; Harmon, D. J.; Welch, K. R. *Anal. Chem.* **1979**, *51*, 1293–1296.
(10) Craig, A. G.; Cullis, P. G.; Derrick, J *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 297–304.
(11) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776–780.
(12) Chait, B. T.; Shpungin, J.; Field, F. H. *Int. J. Mass. Spectrom. Ion Processes* **1984**, *58*, 121–137.
(13) Lattimer, R. P. *Int. J. Mass Spectrom. Ion Processes* **1983/1984**, *55*, 221–232.
(14) Gilliam, J. M.; Landis, P. W.; Occolowitz, J. L. *Anal. Chem.* **1984**, *56*, 2285–2288.
(15) Chan, K. W. S.; Cook, K. D. *Org. Mass Spectrom.* **1983**, *18*, 423–425.
(16) Lai, S. T. F.; Chan, K. W.; Cook, K. D. *Macromolecules* **1980**, *13*, 953–956.
(17) Briggs, D.; Brown, A.; Van Den Berg, J. A.; Vickerman, J. C. *Springer Ser. Chem. Phys.* **1983**, *25*, 162–166.
(18) Campana, J. E.; Rose, S. L. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 483–486.
(19) Lattimer, R. P.; Harris, R. E.; Schulten, H. R. *Rubber Chem. Technol.* **1985**, *58*, 577–621.
(20) Schulten, H. R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231–315.
(21) Mattern, D. E.; Hercules, D. M. *Anal. Chem.* **1985**, *57*, 2041–2046.
(22) Bletsos, I. V.; Hercules, D. M.; Griefendorf, D.; Benninghoven, A. *Anal. Chem.* **1985**, *57*, 2384–2388.
(23) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A.
(24) McCreery, D. A.; Ledford, E. G., Jr.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 1435–1437.
(25) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985** *57*, 520–524.
(26) Brown, E. C.; Kovacic, P.; Wilkie, C. A.; Cody, R. B., Jr.; Kinsinger, J. A. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 453–463.
(27) Wiley, R. H. *Macromol. Rev.* **1979**, *14*, 379–417.
(28) American Society for Testing and Materials, *1985 Annual Book of ASTM Standards*; Philadelphia, PA 1985; Vol. 8.03, 553–561.
(29) Lattimer, R. P.; Schulten, H. R. 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego, CA, May 1985, *Abstr.* 409–410.
(30) Callahan, J. H.; Cook, K. D. 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, May 1984, *Abstr.* 552–553.