the formation of $(CH)_x$ from $(CF_2)_x$ poses interesting mechanistic questions concerning this chemical transformation.

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Registry No. $(CH_3)_3CO_2K$, 865-47-4; I_2, 7553-56-2; benzoin, 119-53-9; sodium naphthalide, 3481-12-7; potassium naphthalide, 4216-48-2.

References and Notes

(1) Costello, C. A; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.
(2) Cervinka, L.; Dousek, F. P.; Janstra, J. *Philos. Mag.* **1985**, *51*, 603 and references therein.
(3) Barker, D. J.; Brewis, D. M.; Dahm, R. H. *J. Mater. Sci.* **1979**, *14*, 749.
(4) Yoshino, K.; Yanagida, S.; Sakai, T.; Azuma, T.; Inuishi, Y.; Sakurai, H. *Jpn. J. Appl. Phys.* **1982**, *21*, L301.
(5) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 2087.
(6) Lefrant, S. *J. Phys. (Paris)* **1983**, *44*, C3-33.
(7) Lichtmann, L. S.; Fitchen, D. B. *Synth. Met.* **1979**, *1*, 130.
(8) Lichtmann, L. S.; Sarhangi, A.; Fitchen, D. B. *Solid State Commun.* **1980**, *36*, 869.
(9) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
(10) Faingold-Murshak, V.; Karvaly, B. *Polym. Commun.* **1985**, *26*, 358.
(11) Wirsen, A.; Flodin, P. *J. Appl. Polym. Sci.* **1978**, *22*, 3039.
(12) Tiziani, R.; Brivio, G. P.; Mulazzi, E. *Phys. Rev. B: Condens. Matter* **1985**, *B31*, 4015.
(13) Vardeny, Z.; Ehrenfreund, E.; Brafman, O.; Horovitz, B. *Phys. Rev. Lett.* **1983**, *51*, 2326.
(14) Kuzmany, H. *Phys. Status Solidi B* **1980**, *97*, 521. Eckhardt, H.; Steinhauser, S. W.; Chance, R. R.; Schott, M.; Silbey, R. *Solid State Commun.* **1985**, *55*, 1075.
(15) Fincher, C. R.; Osaki, M.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B: Solid State* **1970**, *B19*, 4140.
(16) McCarthy, T. J., private communication. Aclar films were obtained from Allied-Signal.
(17) MacDiarmid, A. G.; Heeger, A. J. *Synth. Met.* **1979**, *1*, 101.
(18) Eckhardt, H.; Shacklette, L. W.; Szobota, J. S.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 401.
(19) Tunistra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126.
(20) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.
(21) Whitney, D. H.; Wnek, G. *Polym. Mater. Sci. Eng.* **1985**, *53*, 659.
(22) Shacklette, L. W.; Elsenbaumer, R. L.; Baughman, R. H. *J. Phys. (Paris)* **1983**, *44*, C3-559.
(23) Zannoni, G.; Zerbi, G. *J. Mol. Struct.* **1983**, *100*, 485.
(24) Peluso, A.; Seel, M.; Ladik, J. *Solid State Commun.* **1985**, *53*, 893.

Laser Desorption Time-of-Flight Mass Spectrometry of Low Molecular Weight Polymers

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ABSTRACT: A laser desorption time-of-flight mass spectrometer (LD-TOF-MS) has been used to examine a number of low molecular weight polymers. Laser desorption is provided by a high-power, moderately focused, pulsed CO_2 laser. A time-variable drawout pulse is used to selectively extract lower energy quasi-molecular ions, $[M + K]^+$, and thus reduce the abundances of the fragment ions that are observed. Reliable molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) were calculated from the $[M + K]^+$ ion relative intensities for a series of poly(ethylene glycol) and poly(propylene glycol) samples with oligomer molecular weights up to ~5000. Molecular weight averages determined for a series of poly(ethylene imine) samples were somewhat too low, however; this may be attributed to a thermal fragmentation effect. Two additional low molecular weight polymers with different structures were also qualitatively analyzed. The use of LD-TOF-MS to characterize oligomeric mixtures has been demonstrated.

A number of desorption ionization methods have been used for the direct mass spectral analysis of low molecular weight polymers.[1,2] "Direct" in this sense means that mass spectra are obtained that contain very high abundances of molecular (or quasi-molecular) ions with minimal contribution of ions due to fragmentation/decomposition processes. Methods that have been used, with varying degrees of effectiveness, include field desorption (FD-MS), electrohydrodynamic ionization (EH-MS), ^{252}Cf plasma desorption (PD-MS), laser desorption (LD-MS), fast atom bombardment (FAB-MS), and thermospray (TSP-MS). The major application areas have been (a) structural characterization of oligomeric mixtures (monomer types, end groups, and impurities), (b) identification of chromatographic (GC, LC, and GPC) effluents, and (c) determination of polymer molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$).

Polyglycols has been the class of low molecular weight polymers most often studied by desorption ionization mass spectrometry. Field desorption has been used to examine poly(propylene glycol) (PPG),[3–6] poly(ethylene glycol) (PEG),[5,6] and poly(tetrahydrofuran).[6] In FD-MS analysis, polyglycols generally yield protonated molecular ions $[M + H]^+$ of reasonable intensity, but fragment ions are also prominent, particularly at low masses. Alkali cation attachment is often employed to obtain enhanced quasi-molecular ion spectra. A number of PEG samples have also been analyzed by EH-MS.[7–9] Sodium attachment ions were dominant in EH spectra obtained from NaI/glycerol solutions,[7] and fragment ions were essentially absent.

Two types of laser desorption mass spectrometers have been used to study polyglycols. A commercial LD time-of-flight (TOF) system (LAMMA-1000) yielded useful cation attachment mass spectra for several PEG and PPG batches.[10] The LAMMA system was limited, however, to an effective mass range of only ~1000. PEG and PPG have also been examined with a commercial LD-FT-MS system (Nicolet FTMS-1000).[11,12] In some samples quasi-molecular ions were observed in excess of m/z 7000.[12] Other desorption ionization techniques that have been used to study polyglycols are PD-MS,[13] FAB-MS,[14] and TSP-MS.[15]

The principal practical polyglycol applications have been (a) the general characterization of oligomeric mixtures to determine various end groups[5,12,13] and the composition of copolymers[5] and (b) the determination of molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) for various polyer batches.[6,7,10,12] Desorption ionization mass spectrometry provides a novel and useful means for the *direct* determination of $\bar{M}_n$ and $\bar{M}_w$ values, since the information needed (oligomer molecular weights and relative intensities) is provided directly by the molecular (or quasi-molecular) ion mass spectra. FD-MS, EH-MS, and LD-MS have been particularly effective means for calculating molecular weight distributions of polyglycols, since fragmentation is often much less than that observed in some other methods such as SIMS, FAB-MS, or PD-MS.

Another class of low-mass polymers that has been studied extensively by desorption ionization methods is poly(ethylene imine) (PEI). These polymers are isoelectronic with PEG, but the labile N–H proton introduces an extra measure of complexity to these molecules. Specifically, PEIs have much stronger hydrogen-bonding interactions than PEGs, and these polymers are also normally very highly branched at tertiary nitrogen sites. PEIs have been studied by EH-MS,[16] FD-MS,[17] PD-MS,[18] and LD-FT-MS.[12] Interestingly, molecular weight averages for batches of PEI determined by different desorption ionization methods have varied greatly. For example, in one particular PEI 1200 sample, reported $\bar{M}_n$ values determined by four methods (EH-MS, FAB-MS, FD-MS, and LD-FT-MS) differed by more than a factor of 2.[12,16,17] At this point, the reasons for these inconsistencies are not entirely clear. Excessive fragmentation reactions were a major factor leading to the low FAB-MS values,[17] and hydrogen-bonding interactions contributed to the low values in EH-MS.[16,17] One difficulty with PEI is that unambiguous values of $\bar{M}_n$ and $\bar{M}_w$ are not known for the samples that have been examined. One cannot perform reliable end-group titration, for example, due to branching and the internal labile protons.

In this paper we examine several low molecular weight polymer batches by LD-TOF mass spectrometry.[19,20] The instrument used has a number of features that distinguish it from either the laser microprobe (LAMMA)[10] or the LD-FT-MS[11,12] instruments. Specifically, ion acceleration is initiated with a drawout pulse. Prolonged desorption of ions and neutrals follows the laser pulse, and it has been shown that delaying the drawout pulse has the effect of accelerating ions with lesser amounts of excess internal energy.[20] This provides a means of obtaining spectra in which quasi-molecular ions are enhanced compared to fragment ions and other ions possessing high internal energy.

The principal polymers investigated in this study were several batches of PEG, PPG, and PEI. Spectra obtained with the LD-TOF instrument are compared with those obtained by other desorption ionization methods. The utility of LD-TOF-MS for the general characterization of oligomeric mixtures and the determination of molecular weight averages is demonstrated. Finally, spectra obtained for two commercial low-mass polymers of different structures are reported to demonstrate the general utility of the technique.

Experimental Section

The LD-TOF-MS system has been described in detail elsewhere.[19] A 10.6-μm wavelength CO_2 laser (Tachisto Model 215A) with a pulse width of 40 ns and an energy output of 0.1 J/pulse was used. The mass spectrometer is a CVC Model 2000 TOF instrument with a 1-m flight tube. The laser beam is focused by a 25-cm (10-in.) focal length zinc selenide lens onto a Vespel probe tip approximately 8 in. from the lens. Ions initially accelerated to 3-keV energy are postaccelerated at the end of the flight tube to 12 keV prior to detection. The mass resolution ($M/\Delta M$) is ~200 at m/z 500. Mass spectra following each laser pulse are recorded as analog signals and are digitized with a Le Croy 100-MHz waveform recorder and then stored as 8K channels on a Le Croy 3500 SA signal-averaging system. Time resolutions of 10 or 20 ns were used in these experiments. In operation, a 1-Hz clock pulse triggers the laser and, after a preselected delay time, triggers both the drawout (ion extraction) pulse and the waveform recorder. The cycle is repeated until 20–50 spectra have been accumulated and added in the signal averager. Spectral display, processing, mass calibration, and plotting are carried out on the Le Croy system.

The samples examined were PEG 1450 and 3350 (Sigma Chemical Co.), PPG 790 (Waters Associates no. 41993), PPG 1220 (Waters no. 41994), PPG 2020 (Waters no. 41985), PPG 3000 (Aldrich no. 20,234-7), PEI 600, 1200, and 1800 (Polysciences Inc.), Flectol DS (Monsanto Co.), and Hycar CTB 2000X165 (BFGoodrich Co.). About 10 μg of sample (from 1 μg/μL solutions in methanol) was deposited on a Vespel probe tip. In each case KCl was added to the probe tip to enhance ion formation by K^+ ion attachment. Mass assignments are made by the Le Croy 3500 using the recorded flight times of Na^+, K^+, and Cs^+ for calibration.

Peak intensities for use in the average molecular weight calculations were determined by using software contained in the Le Croy 3500. The program integrates the area under each $[M + K]^+$ peak envelope after drawing a base line between adjacent peak valleys. The integrated areas (N_i) are then used with the isotope-averaged oligomer molecular weights (M_i) to calculate the number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) using the normal equations:

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

and

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

While no detailed study of molecular weight average as a function of delay time was carried out, it was found empirically that the $\bar{M}_n$ value increases as the delay time is increased. At a delay time of ~15 μs, the molecular weight distribution for a particular polymer leveled off and became constant. A delay time of 15–20 μs was found to be optimal in terms of obtaining the best $[M + K]^+$ ion distribution and focusing.

Results and Discussion

PEG, PPG, and PEI Spectra. LD-TOF mass spectra are included for PEG 1450 (Figure 1), PEG 3350 (Figure 2), PPG 1220 (Figure 3), PPG 3000 (Figure 4), PEI 1200 (Figure 5), and PEI 1800 (Figure 6). Only those portions of the spectra covering the molecular ion regions are displayed, but fragment ions were of low relative intensity at lower masses. The major low-mass ion in all spectra was K^+. For PEG (Figures 1 and 2), the major peak envelopes correspond to $[M + K]^+$ ($m/z = 44n + 57$). For PEG the only fragment ions that are readily discernible fall in the series ($m/z = 44n + 39$). Other minor fragment ion series could well be present, but these are not resolved by the TOF analyzer. The ($m/z = 44n + 39$) peaks can be formally designated as "water loss" ions (i.e., $[M - H_2O +$

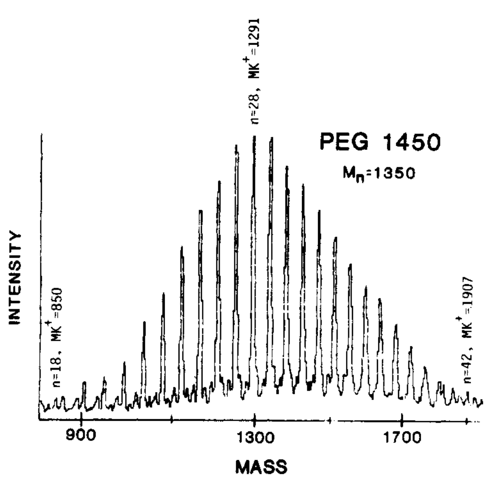


Figure 1. LD-TOF mass spectrum of PEG 1450.

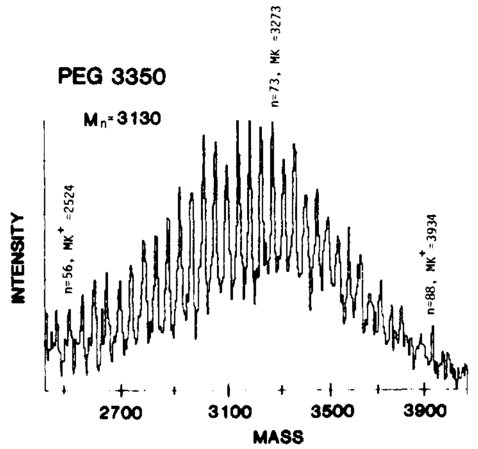


Figure 2. LD-TOF mass spectrum of PEG 3350.

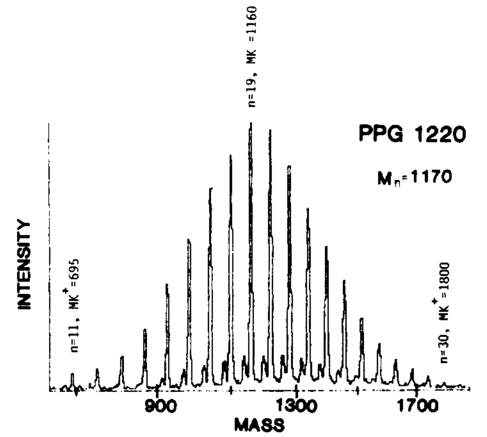


Figure 3. LD-TOF mass spectrum of PPG 1220.

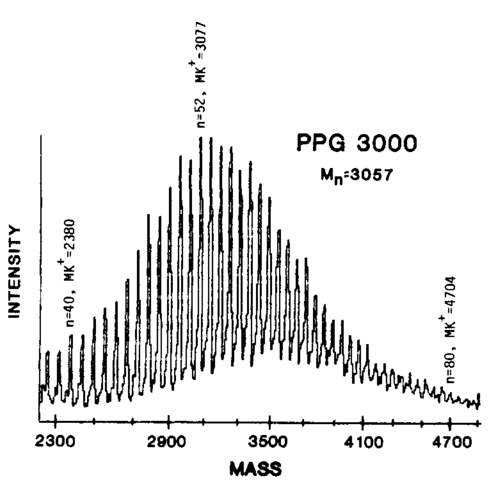


Figure 4. LD-TOF mass spectrum of PPG 3000.

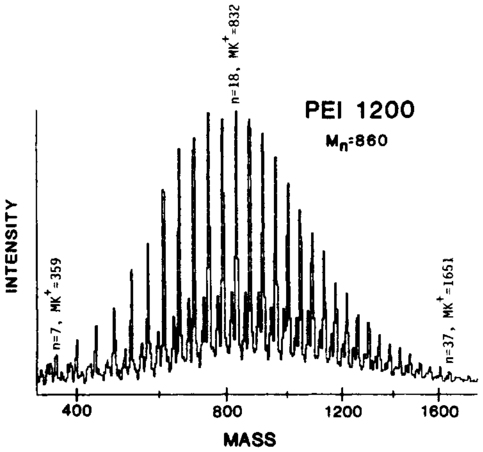


Figure 5. LD-TOF mass spectrum of PEI 1200.

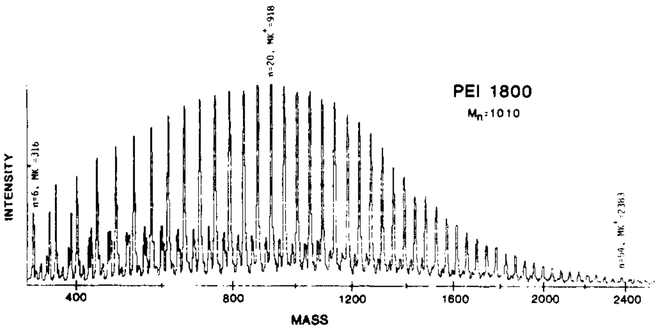
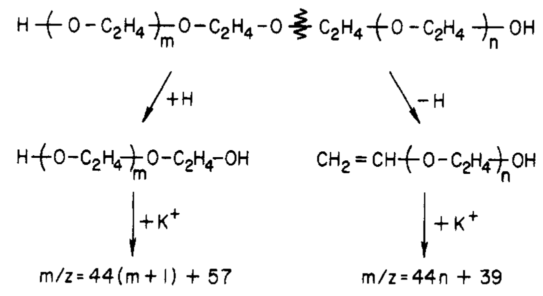
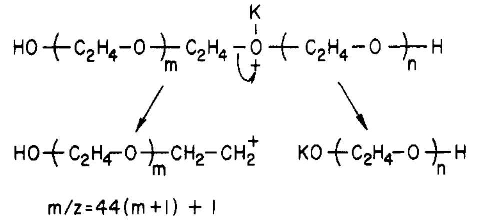


Figure 6. LD-TOF mass spectrum of PEI 1800.

Scheme I



Scheme II



K]$^+$), but their formation is probably more correctly represented by the reaction given in Scheme I. Scheme I suggests that *thermal decomposition* (pyrolysis) of the polymer chain proceeds via a homolytic cleavage pathway. Pyrolysis products (neutral macromolecules) can then ionize via cation attachment. Note that this process creates lower molecular weight PEG oligomers as well as terminally unsaturated oligomers. Thus if this process proceeds to any great extent, observed intensities of lower mass oligomers will tend to be too large. This effect was noted

Table I
Molecular Weight Averages for PEG, PPG, and PEI

polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	method	ref
PEG 1450	1350	1380	1.02	LD-TOF-MS	this work
	1384	1404	1.01	LD-FT-MS	12
	1349			EGT[a]	12
PEG 3350	3130	3160	1.01	LD-TOF-MS	this work
	3160	3189	1.01	LD-FT-MS	12
	3297			EGT	12
PPG 790	730	750	1.03	LD-TOF-MS	this work
	805	835	1.04	FD-MS	6
	819	855	1.04	FD-MS	6
	710	741	1.04	FAB-MS	14
	790		~1.05		*b*
PPG 1220	1170	1205	1.03	LD-TOF-MS	this work
	1240	1280	1.03	FD-MS	6
	1190	1220	1.03	FD-MS	6
	1064	1110	1.04	FAB-MS	14
	1220				*b*
PPG 2020	1920	1960	1.02	LD-TOF-MS	this work
	1930	1980	1.03	FD-MS	6
PPG 3000	3057	3110	1.02	LD-TOF-MS	this work
PEI 600	590	640	1.08	LD-TOF-MS	this work
	685	742	1.08	LD-FT-MS	12
	553	583	1.05	FD-MS	17
	557	627	1.13	FD-MS	17
	513	585	1.14	FAB-MS	17
	399			EH-MS	16
PEI 1200	860	925	1.08	LD-TOF-MS	this work
	1137	1226	1.08	LD-FT-MS	12
	739	850	1.15	FD-MS	17
	766	860	1.12	FD-MS	17
	551	636	1.15	FAB-MS	17
	505			EH-MS	16
PEI 1800	1010	1150	1.14	LD-TOF-MS	this work

[a] End-group titration. [b] Data supplied by Waters Associates.

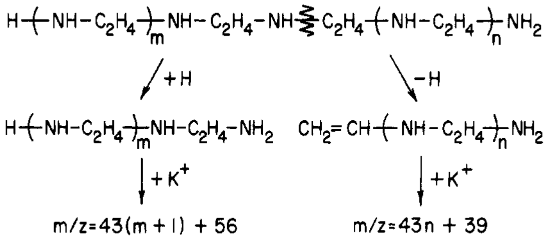
in the FAB-MS analysis of PEG and PPG.[14]

Unimolecular decomposition of $[M + K]^+$ ions might be expected to follow a heterolytic cleavage pathway as shown in Scheme II. This type of ion decomposition is rather prominent in FAB mass spectra of PEG,[14] but Scheme II does not appear to be a major factor during LD-MS experiments.

The spectra for PPG (Figures 3 and 4) are analogous to those for PEG. The major ions are $[M + K]^+$ ($m/z = 58n + 57$), and minor "water loss" ions ($m/z = 58n + 39$) are also observed. Again the term "water loss" is a formal designation, and the actual mechanism should be analogous to that shown for PEG in Scheme I. The water loss ions are unresolved from $[M + K]^+$ for the higher mass oligomers (Figure 4). Similarly, PEI (Figures 5 and 6) shows major ions due to $[M + K]^+$ ($m/z = 43n + 56$) and less abundant "ammonia loss" ions ($m/z = 43n + 39$).

Molecular Weight Averages. LD-TOF-MS $\bar{M}_n$ and $\bar{M}_w$ values for the various PEG, PPG and PEI samples are given in Table I. Values determined by other methods, when available, are also included. We will first examine the results for PEG and PPG. In cases where comparisons can be made for the same polymer batch, it is evident that LD-TOF-MS, LD-FT-MS, FD-MS, and classical methods (e.g., end-group titration) all give very similar results. The average deviation for $\bar{M}_n$ between any two of these methods is ~4%, which is certainly within the experimental error of the measurements. Although EH-MS results are not available for these particular batches, previous work indicates that this method also gives reliable molecular weight averages for lower mass polyglycols.[7] The FAB-MS molecular weight averages are somewhat lower than the results from the other methods. This is due to extensive fragmentation reactions (see Scheme I) that create lower mass oligomers during the bombardment process.[14] The lower mass oligomers are thus weighted too heavily in the average molecular weight calculations.

Scheme III



The results for PEI (Table I) differ widely among the various methods. Note that the order of increasing molecular weight is EH < FAB < FD < LD-TOF < LD-FT. First, a major factor leading to the low values determined by EH-MS is probably *hydrogen bonding*.[16,17] Extensive hydrogen-bonding interactions in solution create an EH sampling bias so that the lower mass oligomers (with less hydrogen bonding) are extracted more efficiently. Hydrogen bonding would be more important for polyimines[16] than for polyglycols.[7] Also EH-MS, which is a less energetic ionization method, would be more susceptible to hydrogen-bonding effects than most (if not all) other desorption ionization methods.

The low FAB molecular weight averages can also be readily explained. In FAB-MS the lower oligomer intensities tend to be too high due to *thermal fragmentation* reactions induced by the fast atom beam.[17] A probable mechanism for this, shown in Scheme III, is analogous to that for PEG in Scheme I. Scheme III provides one means of forming lower mass oligomers in situ; these oligomer "artifacts" will cause the lower mass portion of the spectrum to be weighted too heavily in the calculation of the molecular weight averages.

The FD-MS molecular weight averages for PEI are apparently also somewhat low, and this is more difficult to explain. Unimolecular ion decomposition might be one factor to consider, but it is not clear to us that ion fragmentation is more extensive for PEI[17] than it is for polyglycols.[3-6] It seems more likely that a combined *hydrogen bonding/thermal fragmentation* (pyrolysis) effect is responsible for the low FD molecular weight averages. Hydrogen bonding will tend to keep the higher mass oligomers on the field emitter for a longer period of time than might otherwise be expected. Thus, relatively higher emitter temperatures will be required for desorption of PEI compared, for example, to PEG or PPG, which have relatively little hydrogen bonding. At higher emitter temperatures, and perhaps under the influence of the field, some homolytic cleavage of macromolecules may be induced (Scheme III). These pyrolytic reactions will produce lower mass oligomers in situ while at the same time reduce the abundances of the higher mass oligomers. The effect in FD-MS is certainly much less pronounced than it is in FAB-MS,[17] but it does seem to be a logical explanation for the lower observed FD-MS molecular weight averages.

Finally, we can consider the LD-MS results. Since the LD-FT-MS molecular weight averages[12] are the closest to the values reported by the manufacturer, this technique at first glance appears to give superior results when compared to the other desorption ionization methods (Table I). It is especially puzzling that the LD-FT numbers differ by such a large amount from the LD-TOF results. To begin with, the method used for laser desorption is very similar in both instruments. Thus differences in the mechanism of ion formation do not appear to be significant. Also, since the TOF-MS and FT-MS systems have been shown to give reliable molecular weight averages for

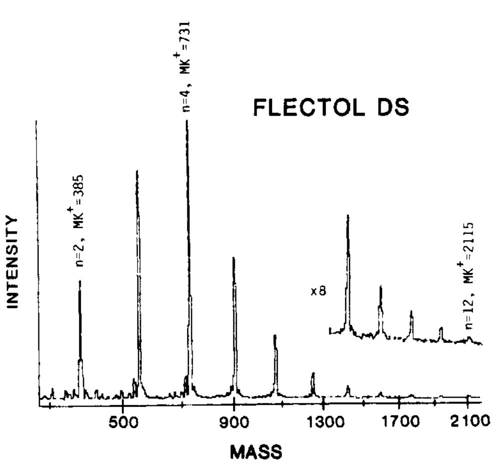


Figure 7. LD-TOF mass spectrum of Flectol DS (poly-TMDQ).

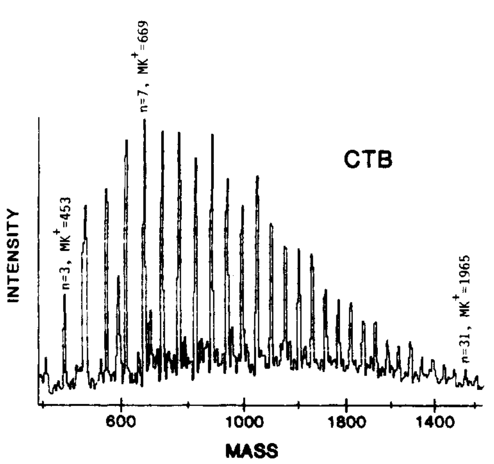
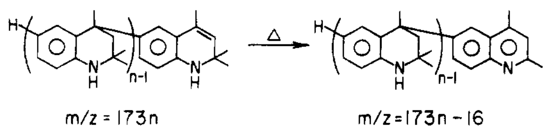


Figure 8. LD-TOF mass spectrum of Hycar CTB 2000X165.

polyglycols (Table I), differences in the mass separation and detection methods should not be expected to introduce any appreciable error. This leaves *ion sampling* as the probable cause for the observed differences, and the two LD-MS instruments vary considerably in this respect. The FT-MS cell, with a trapping voltage of ~1 V, only captures those ions possessing very low internal and translational energies. Neutral molecules, nearly all fragment ions, and higher energy quasi-molecular ions are eliminated at the outset. Also, ion excitation delay times of at least several milliseconds are typically used to reduce the cell pressure, and this may tend to further reduce high-energy ions. Those quasi-molecular ions that remain trapped in the cell have little excess internal energy, and thus they are unlikely to fragment. It is this low energy ion trapping feature of FT-MS that leads to mass spectra which show minimal evidence of fragmentation. Laser desorption is an energetic vaporization/ionization process. A very useful feature of the combined LD-FT-MS approach is that the trapping cell serves an an "energy filter" to eliminate nearly all of the higher energy fragments.

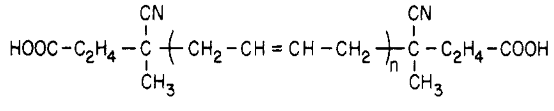
LD-TOF-MS also has a type of energy filter in the form of its time-delayed drawout pulse. A longer time delay results in the extraction of ions possessing lower internal energies. Most of the high-energy neutrals and ions escape from the source region during the first few microseconds after the laser pulse. This "energy filter" in LD-TOF-MS is apparently not quite as effective as that in LD-FT-MS. A comparison of LD mass spectra for PEI 1200 shows that "ammonia loss" ions are 3–4 times greater in relative abundance for LD-TOF-MS (Figure 5) as compared to LD-FT-MS.[12] This suggests, via the reaction mechanism in Scheme III, that lower mass oligomers might be relatively more abundant in LD-TOF-MS than in LD-FT-MS. This in turn will lead to differences in the calculated molecular weight averages.

Other Examples. The LD-TOF mass spectrum of Flectol DS is given in Figure 7. This material is an oligomeric rubber antioxidant formed by the acid-catalyzed polymerization of 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ); TMDQ is a condensation product of aniline and acetone.[21,22] The spectrum is rather clean; the major peaks observed are $[M + K]^+$ ions ($m/z = 173n + 39$). The only readily discernible fragment ions are "methane loss" peaks at ($m/z = 173n + 23$). These are easily formed thermally, since the product is a stable quinoline species:



Oligomer quasi-molecular ions are observed up to the dodecamer (MW = 2076). The average molecular weight of this material was not calculated and is not known, but the ability of LD-TOF-MS to provide a good qualitative characterization of this low-mass polymer is demonstrated.

The LD-TOF mass spectrum of CTB 2000X165 is shown in Figure 8. This is a reactive liquid polymer (carboxyl-terminated *cis*-1,4-polybutadiene) prepared free radically with the initiator 4,4′-azobis(4-cyanopentanoic acid) (ADVA):[23]



$$HOOC{-}C_2H_4{-}\underset{CH_3}{\overset{CN}{C}}{-}\left[CH_2{-}CH{=}CH{-}CH_2\right]_n{-}\underset{CH_3}{\overset{CN}{C}}{-}C_2H_4{-}COOH$$

$m/z = 54n + 252$

The major LD-TOF ions are $[M + K]^+$ for the numerous oligomers ($m/z = 54n + 291$). Some fragmentation is evident, but we have not studied the fragment ions in any detail. The $\bar{M}_n$ value for this polymer is ~3000;[23] thus it is clear that the lower mass oligomers desorb preferentially. Nevertheless, the LD-TOF spectrum provides a good qualitative characterization of the polymer.

Conclusion

Our results show that good qualitative charcterizations of various low molecular weight polymers can be obtained by LD-TOF-MS. The use of a time-delayed drawout pulse enables one to selectively extract lower energy quasi-molecular ions and thus reduce the abundances of fragment ions that are observed. Reliable molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) could be calculated from the $[M + K]^+$ ion relative intensities for a series of PEG and PPG samples with oligomer masses up to ~5000. Molecular weight averages determined for a series of PEI samples were somewhat too low, however. This is attributed to a thermal fragmentation effect in which lower oligomers are created in situ via homolysis of backbone C–N bonds. The time-delayed drawout pulse helps to reduce the amounts of these oligomer "artifacts" that are accelerated to the detector, but the delay is not capable of eliminating these thermally produced fragments entirely.

Two additional low molecular weight polymers with different structures were also qualitatively analyzed by LD-TOF-MS. These were poly-TMDQ and carboxyl-terminated polybutadiene (CTB). While accurate molecular weight averages were not determined, the use of LD-TOF-MS to qualitatively characterize these oligomeric mixtures was demonstrated.

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Registry No. PEG, 25322-68-3; PPG, 25322-69-4; PEI, 9002-98-6; flectol DS, 26780-96-1.

References and Notes

(1) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.
(2) Lattimer, R. P.; Harris, R. E.; Schulten, H.-R. *Rubber Chem. Technol.* **1985**, *58*, 577.
(3) Matsuo, T.; Matsuda, H.; Katakuse, I. *Anal. Chem.* **1979**, *51*, 1329.
(4) Neumann, G. M.; Cullis, P. G.; Derrick, P. J. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1980**, *35A*, 1090.
(5) Saito, J.; Toda, S.; Tanaka, S. *Shitsuryo Bunseki* **1980**, *28*, 175.
(6) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776.
(7) Lai, S.-T. F.; Chan, K. W. S.; Cook, K. D. *Macromolecules* **1980**, *13*, 953.
(8) Chan, K. W. S.; Cook, K. D. *Org. Mass Spectrom.* **1983**, *18*, 423.
(9) Chan, K. W. S.; Cook, K. D. *Macromolecules* **1983**, *16*, 1736.
(10) Mattern, D. E.; Hercules, D. M. *Anal. Chem.* **1985**, *57*, 2041.
(11) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985**, *57*, 520.
(12) Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 1255.
(13) Chait, B. T.; Shpungin, J.; Field, F. H. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 121.
(14) Lattimer, R. P. *Int. J. Mass Spectrom. Ion Processes* **1983/1984**, *55*, 221.
(15) Goodley, P. C., private communication.
(16) Callahan, J. J.; Cook, K. D. 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, May 27–June 1, 1984, p 552.
(17) Lattimer, R. P.; Schulten, H.-R. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 227.
(18) Robbins, R. C.; Alai, M.; Demirev, P.; Cotter, R. J. 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego, May 26–31, 1985, p 403.
(19) van Breemen, R. B.; Snow, M.; Cotter, R. J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 35.
(20) Tabet, J.-C.; Cotter, R. J. *Anal. Chem.* **1984**, *56*, 1662.
(21) Lattimer, R. P.; Harmon, D. J.; Welch, K. R. *Anal. Chem.* **1979**, *51*, 1293.
(22) Lattimer, R. P.; Hooser, E. R.; Zakriski, P. M. *Rubber Chem. Technol.* **1980**, *53*, 346.
(23) Diem, H. E.; Harmon, D. J.; Komoroski, R. A.; Pausch, J. B.; Bertsch, R. J. *Adv. Chem. Ser.* **1984**, *No. 208*, 65.

Notes

Characterization of the Soluble Phase beyond the Gel Point

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The physicochemical properties of branched macromolecules have been a subject of much interest in polymer science. Because of its complexity, the process of gelation and the chemistry of the sol fraction that the product contains well beyond the gel point have been the objects of relatively little experimental research. One line of work, arising from Gordon's team, has been devoted to correlating molecular parameters of the critically branched state of matter with those calculated from the Cascade theory.[1-6] The experimental materials were the stabilized macromolecules that appear just before and just after the gel point in the polycondensation of 1,3,5-benzenetriacetic acid with 1,10-decamethylene glycol (BTA/DMG). This combination of monomers has been a particularly good choice because it has given minimum deviations from the assumptions of the classical gelation theory.[5-7]

Beyond these experiments on the critically branched state of matter, there is no record of attempts to exploit the near ideality of BTA/DMG polymerization in order to investigate other features of gelation. The molecular properties of the soluble phase and the way they change as gelation advances well beyond the gel point have not been experimentally examined with an ideal system.

Therefore, as an extension of our efforts[8] to characterize the soluble phase, fractions at various extents of polymerization of BTA/DMG beyond the gel point were isolated, and their viscosities and weight-average molecular weights were measured.

The relative changes of the densities and diameters of these macromolecules at various stages of the reaction beyond the gel point were calculated, thus providing more information for this rather important region of the process.

Table I
Molecular Weights, Viscosities, and Structural Parameters of the BTA/DMG Sol Fractions as a Function of Conversion beyond the Gel Point

convn (p)	W_S[c]	$\bar{M}_w \times 10^{-5}$	$[\eta]$, dL g^{-1}	equiv dens (ρ_{equ}), g mL^{-3}	equiv diam (d_{equ}), Å
0.7205[a]		8.19	0.206[a]	0.121	277
0.7206[a]		4.39	0.200[a]	0.125	222
0.7226[a]		1.75	0.130[a]	0.192	142
0.7260	0.752	1.45	0.166[b]	0.150	144
0.7670	0.347	0.18	0.199[b]	0.210	66
0.8090	0.130	0.16	0.149[b]	0.167	68

[a] Reported by Peniche-Covas et al.[5] [b] Measured at 25 °C in methyl ethyl ketone. [c] Soluble fraction, i.e., (wt sol)/(wt (sol + gel)).

Results and Discussion

Intrinsic viscosities of three sol fractions of the BTA/DMG polycondensation in the region just beyond the gel point have been reported by Peniche-Covas et al.[5] In order to obtain additional points, the viscosity numbers (Table I) of sols isolated at conversions well beyond the gel point were measured at 25 °C at four different concentrations in methyl ethyl ketone.

It is immediately apparent that these intrinsic viscosities are unusually low. The low intrinsic viscosities reported here indicate that the molecules are likely to have a highly branched structure.

Further evidence of extensive branching is seen in the small dependence of intrinsic viscosity on molecular weight (Figure 1). The exponent α and constant K of the Mark–Houwink equation were thus found to be 0.15 and 11.2, respectively ($K = 0.112$ if $[\eta]$ is expressed in deciliters per gram). The unusually low value of α indicates that the highly branched structure of these polymers confers con-