Structural Analysis of Polyoxyalkyleneamines by Matrix-Assisted Laser Desorption/Ionization on an External Ion Source FT-ICR-MS and NMR

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ABSTRACT: Matrix-assisted laser desorption/ionization (MALDI) and Fourier-transform ion cyclotron mass spectrometry (FT-ICR-MS) are combined for the characterization of polyoxyalkyleneamines. ^{1}H and ^{13}C NMR data are used to confirm and quantify structural assignments. Characterization of the molecular weight distribution, chemical composition distribution, and end group distribution of amine-terminated (co-)polymers of ethylene oxide and propylene oxide is rather complex because the convolution of these three entities yields an ensemble of structurally related molecules which is hard to characterize by conventional analytical techniques. In this study MALDI FT-ICR-MS is used to resolve intact, Na^{+} cationized, oligomer ions in the mass range from m/z 500 to 3500. This revealed the presence of various compositional distributions in the polyoxyalkyleneamines. The individual compound masses in the molecular weight distributions were measured with a mass accuracy of <20 millimass units, allowing end group and repeat unit determination with an accuracy of better than 50 millimass units. NMR is used to measure the average end group distribution to provide insight in conformational differences. In this respect, FT-ICR-MS data and NMR data are complementary. The combined results yield detailed information about chemical composition distributions of polyoxyalkyleneamines that hitherto it was not possible to obtain with either technique separately.

Introduction

Polyoxyalkeneamines are water-soluble amine-terminated low molecular weight (MW < 6000) polymers or copolymers of ethylene oxide (EO) and propylene oxide (PO).[1] These polyether amines are of considerable commercial importance and are used in numerous applications as emulsifiers, epoxy curing agents, lubricants, and fuel additives and to a large extent as building blocks for polymeric systems such as polyurethane and polyurea.

Diamine polyethers are often used as flexible building blocks for the synthesis of elastomeric polyurea.[2] Bulk synthesis of block copolyurea is performed by reacting a liquid polyisocyanate with a mixture of an amine functionalized polyether and an aromatic diamine.[3] The polyurea thus formed consists of variable rigid and soft segments which can be tailored for specific applications. Within this context, it is highly desirable to obtain detailed knowledge of the molecular weight distribution, chemical composition distribution, and end group composition of the polyoxyalkeneamines, as these entities influence the elasticity and viscoelasticity of the polyurea end-product. Furthermore, monoamine and diamine functionalized polyols may contain fractions of undesired end groups which lead to early termination of the polymerization process.

During recent years, matrix-assisted laser desorption and ionization (MALDI) in combination with mass spectrometry has emerged as one of the most useful and straightforward polymer characterization methods.[4,5] Since the introduction of MALDI by Tanaka and coworkers[6] and by Karas and Hillenkamp[7] in 1988, the technique has evolved as a soft method for the volatilization and ionization of a wide range of intact molecules such as peptides, proteins, oligosaccharides, and synthetic polymers. Several reviews illustrate the continually widening scope of MALDI applications.[4,8,9,10] The increasing importance of MALDI mass spectrometry in synthetic polymer chemistry has been driven primarily by its ability to provide molecular weight data of high molecular mass materials that cannot be obtained by methods such as size-exclusion chromatography (SEC), light scattering, and osmometry.

Despite the success of MALDI, the development of the proper MALDI methodology is still largely empirical.[4,11] Samples are prepared by mixing the analytes with an excess of matrix molecules prior to analysis. MALDI is performed by laser desorption of the analytes from a solid matrix. Postulated models suggest that inefficient vibrational energy coupling between the laser-excited matrix molecules and the analytes prevents energy transfer.[12,13] This results in vaporization of the matrix molecules which carry intact analyte molecules of low internal energy into the gas phase. Ionization of the analytes occurs as a result of adduct formation with cations, which are present in the matrix−analyte mixture. Using the MALDI method, intact proteins with masses exceeding 200 000 Da have been successfully ionized.[8,14]

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Nowadays, MALDI is mainly performed on relatively inexpensive commercial benchtop time-of-flight (TOF) mass spectrometers. These systems provide a high mass range over which polymers can be analyzed, up to 1.5 million Da,[15] and high sensitivity. The ability of MALDI−TOF mass spectrometry to provide accurate molecular weight distributions of polymers such as poly(ethylene glycol), poly(methyl methacrylate), poly(styrene), nylon, poly(ethylene terephthalate), poly(carbonate), and poly(ester) has been given considerable attention.[4,5,15−22] However, the limited resolution and mass accuracy of MALDI−TOF mass spectra, as a result of the initial spatial and velocity distributions of the MALDI-generated ions, limits the amount of detail obtained for polymer characterization. Recently, various research groups have shown that the performance of MALDI−TOF mass spectrometry systems improves significantly by the implementation of delayed ion extraction methods.[23,24]

The successful interfacing of MALDI and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is a new development for the characterization of polymers. The many advantages of FT-ICR-MS include unequivocally high mass resolving power, high mass accuracy, and the possibility to store, isolate, and manipulate ions.[25,26] The potential of MALDI FT-ICR-MS has been demonstrated mainly for the analysis of peptides and proteins.[27,28] So far, only a few research groups have exploited FT-ICR-MS for the characterization of synthetic polymers. Wilkins and co-workers determined the molecular weight distributions of several poly(ethylene glycol) samples containing oligomers with masses covering a 10 kDa mass range, using FT-ICR-MS.[29,30] In previous studies, Boon and co-workers showed the feasibility of FT-ICR-MS for the determination of end group functionality in poly(ethylene glycol) samples.[31,32]

In this study, the advantages of MALDI and FT-ICR-MS are combined for the characterization of polyoxyalkyleneamines. In order to screen performance differences between different batches of these polymers, it is highly desired to use techniques that yield accurate mass data over a broad molecular weight range and facilitate a high sample throughput. In light of this, merits and limitations of the data produced with MALDI FT-ICR-MS are discussed and compared with those of ^{1}H and ^{13}C NMR data.

Experimental Section

MALDI FT-ICR-MS. The MALDI experiments are performed on a modified Bruker APEX 7.0e FT-ICR-MS (Fällanden, Switzerland) equipped with a 7-T magnet and an in-house designed external ion source. Instrumental and experimental details have been published, previously.[31,33] Data acquisition control and processing is performed using Bruker XMASS software on a SGI Indigo R4000 UNIX-based workstation in conjunction with an ASPECT X32/4 UNIX computer.

Samples for the MALDI experiments are deposited on a stainless steel probe which is inserted into the external ion source through a vacuum lock. The ion source is pumped to typically 1×10^{-7} mbar, and the pressure maintained in the ICR-cell region is $<1 \times 10^{-10}$ mbar. A Photon Technology (South Brunswick, NJ) PL23000 nitrogen laser is used to generate ions during the MALDI process. The laser produces 337.1 nm laser pulses with an energy of 1.3 mJ and a pulse length of 600 ps. The laser beam is focused onto the probe tip at an incidence angle of 45° with a spot size of approximately 4.5 mm^2. The energy transmitted per pulse measured inside the ion source (0.48 mJ) results in a fluence of 10.6 mJ/cm^2 (which corresponds to a power density of 17.5 MW/cm^2) on the MALDI target.

The ions produced in the source are transferred by the standard Bruker electrostatic ion optics to the ICR-cell. The ions are extracted from the ionization region using a potential difference of approximately 10 V between the source housing and the first extraction plate. Subsequently, the ions are accelerated to 3 keV to prevent radial ejection in the inhomogeneous stray field of the magnet. After deceleration to approximately 1 eV, the ions are trapped in the electrostatic potential well between two trap electrodes in the Bruker Infinity ICR-cell which is centered in the homogeneous field of the 7-T superconducting magnet.

The timing sequence used for the MALDI experiments starts with a quench pulse that removes all ions from the ICR cell. This is followed by a transistor−transistor logic (TTL) pulse to trigger the laser. At the same time the front trapping electrodes are biased such that, temporarily, a channel in the electrostatical potential well is created, allowing the ions to enter the cell. The rear trapping electrode remains at typically 3.5 V. After a variable period of time, corresponding to the time of flight of the ions in the mass range of interest, the front trapping electrode is set to 2.5 V in order to confine the ions in the ICR cell. The asymmetry in the trapping field is introduced because it gives the optimal signal in our experiments. Subsequently, the trapped ions are coherently excited to a higher radius by a frequency sweep (chirp) excitation from a programmable frequency synthesizer. To acquire a mass spectrum, the ion-image-current signals on the detection electrodes are digitized by a 12-bit, 20 MHz analog-to-digital converter and stored in a 128 Kbyte fast memory. Discrete Fourier transformation of this time domain signal followed by magnitude calculation yields a frequency spectrum. This frequency spectrum is subsequently converted into a mass spectrum using the cyclotron relation $\omega = qB/m$. All spectra shown are zero-filled to 256 Kbytes. All mass spectra were obtained in the positive ion mode and externally calibrated using a poly(ethylene glycol) 1000. For the calculation of the actual mass of the ions with a given elemental composition, we use the atomic masses tabulated in the 1983 atomic mass table composed by Wapstra *et al.*[34]

MALDI Sample Preparation. The Jeffamine polyoxyalkeneamines M-2070, D-2000, and ED-2001 (Texaco Chemical Company) are used without purification. 2,5-Dihydroxybenzoic acid (Sigma Chemical Co., Bornem, Belgium) is used as the MALDI matrix. The MALDI samples were prepared by mixing a 1 M 2,5 dihydroxybenzoic acid solution in ethanol with an analyte solution in ethanol in a molar ratio of 2000:1. The analyte−matrix solution was deposited onto a stainless steel probe tip by using an electrospray setup. In this setup a syringe pump model 55-1111 (Harvard Apparatus, Kent, U.K.) is used to deliver 0.30 mL/h to a stainless steel capillary (15 cm × 180 μm, i.d.). This capillary is electrically insulated from the pump with polyether ether ketone (PEEK) tubing (25 × 180 μm) and is typically set to 4 kV. The MALDI probe tip is located about 7 mm behind the capillary and is set to ground potential. Approximately 0.1 mL of analyte−matrix solution is consumed during deposition onto the stainless steel insertion probe.

^{1}H and ^{13}C NMR. NMR spectra of the Jeffamine ED-2001 sample were obtained using a Bruker AM400 NMR spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The solvent for ^{1}H NMR was chloroform-*d*. Initially the ^{13}C NMR spectrum was obtained in chloroform-*d* as well, but this produced severe overlap in the region between 65 and 80 ppm. Much better peak separation was obtained in a 3:1 (v/v) mixture of deuterated hexafluoro-2-propanol (HFI-d_2) and chloroform-*d*. The carbon chemical shifts, presented in Table 3, are measured in this solvent. The same solvent was used for the distortionless enhancement by polarization transfer (DEPT) measurements. TMS was used as internal reference for ^{1}H and ^{13}C NMR.

NMR spectra of the Jeffamine M-2070 sample were obtained using a Bruker ARX 400 spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Spectra were obtained in hexafluoro-HFI-d_2 and chloroform-*d* (3:1 v/v).

Materials. The Jeffamine polyoxyalkeneamines M-2070, D-2000, and ED-2001 are commercially available (Texaco Chemical Company). According to the Texaco Chemical Company data sheet (SC-024 102-0411) , the Jeffamine monoamines are designated as the M series and are prepared by reaction of a monohydric alcohol initiator with EO and PO, followed by conversion of the resulting terminal hydroxyl group to an amine. M-series products have the structure $CH_3O-(C_2H_4O)_m(C_3H_6O)_n-C_3H_6NH_2$. The D-series products are amine-terminated polypropylene glycols with the general structure $H_2N-(C_3H_6O)_n-C_3H_6NH_2$. The ED-series are copolymers of EO and PO and have the general structure $H_2N-(C_2H_4O)_m-(C_3H_6O)_n-C_3H_6NH_2$. The number designation after the letters M, D, and ED represents the approximate molecular weight.

Results and Discussion

Molecular Weight Distributions. The use of an external ion source design for FT-ICR-MS facilitates the implementation of a wide range of ionization techniques because problems with gas sample load during the ionization procedure are reduced by differential pumping of the mass spectrometry system. It is well-known that the use of pulsed ionization techniques on an external ion source results in a significant time-of-flight effect during transport of the ions from the ion source to the ICR-cell.[30] MALDI-generated ions have an identical mass independent velocity distribution.[35] However, postacceleration of the ions to a given kinetic energy adds a mass dependent velocity component ($E_{kin} = {}^1/_2mv^2$), and the ions are separated in a time proportional to the square root of their mass. Consequently, higher mass ions require longer ion accumulation times in the ICR-cell (gated trapping times) than lower mass ions. Therefore, to analyze the complete molecular weight distribution of a disperse synthetic polymer, several measurements at different trapping times need to be performed.

Dey *et al.* developed a procedure to reconstruct the complete molecular weight distribution of a polymer using MALDI on an external ion source FT-ICR-MS.[30] In this method, a summed mass spectrum was obtained by adding the corresponding series of time domain data sets, acquired at systematically increased gated trapping times. The resulting signal averaged composite time domain transient was Fourier transformed and converted into a mass spectrum. In our experience, addition of partly overlapping mass spectra (time-of-flight segments) may lead to some skewing of the reconstructed molecular weight distribution due to overestimation of the most abundant ions (middle of the molecular weight distribution).[36] In the present study, the time domain signals, measured at different trapping times, are directly transformed into mass spectra and the complete molecular weight distribution of the polymer is reconstructed by overlaying the spectra. Using this method, representative molecular weight distributions of the polyoxyalkeneamines are obtained because the intensity of each individual oligomer in the reconstructed molecular weight distributions corresponds to its maximum intensity, obtained at a trapping time where it is most efficiently confined in the ICR-cell.

An example of the time-of-flight effect is shown in Figure 1. In Figure 1, the measured molecular weight distributions of the Jeffamine ED-2001 diamine polymer are depicted as a function of the trapping time. In this experiment, the gated trapping time was incremented with 100 μs steps from 600 to 1400 μs in nine separate measurements. With trapping times larger than 1500 μs no ions were detected. Avoiding trapping times shorter than 500 μs proved to be advantageous because

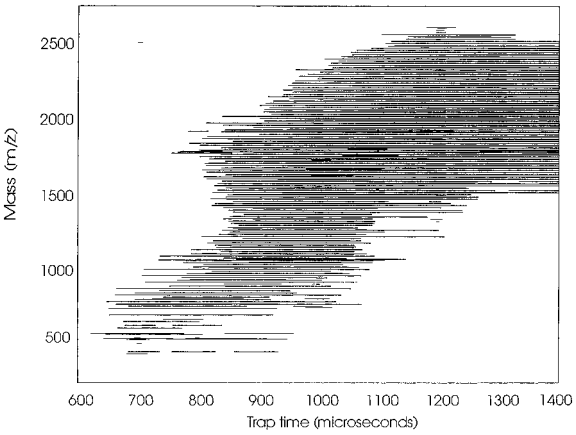


Figure 1. Contour plot displaying the time-of-flight distributions of the MALDI generated ions of Jeffamine ED-2001, as a function of the gated trapping time (ion accumulation time in the ICR-cell). For this measurement the gating time was varied from 600 to 1400 μs in 100 μs intervals. For each individual spectrum 50 laser shots were coadded.

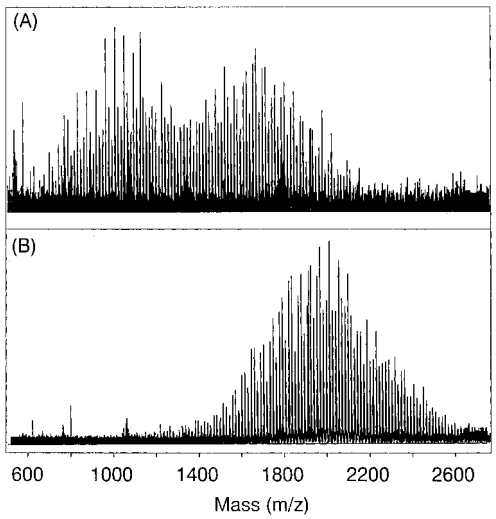


Figure 2. MALDI FT-ICR-MS spectra of Jeffamine ED-2001, measured at a trapping time of 900 μs (A) and 1200 μs (B).

no significant abundance of polyether ions was detected and trapping of matrix ions in the ICR-cell is prevented. Figure 2 illustrates that the MALDI FT-ICR-MS broad-band spectrum of the Jeffamine ED-2001, obtained at a gated trapping time of 900 μs, covers a molecular weight distribution beginning with the sodiated oligomer of m/z 710 up to m/z 2018, while the broad band spectrum recorded at a gating time of 1200 μs covers a molecular weight distribution ranging from m/z 1357 to 2604. Figures 1 and 2 clearly demonstrate that the distortion of the molecular weight distribution due to the different flight times of the ions is strongest at low m/z values. Similar results were obtained for the other Jeffamine polymers. It is obvious that careful selection of trapping times is crucial to avoid misinterpretation of molecular weight distributions when using an external ion source FT-ICR-MS system with a pulsed ionization technique.

The reconstructed total molecular weight distributions of all three polyoxyalkeneamine samples are shown in Figure 3. All three samples show a bimodal molecular weight distribution pointing to contamination with other polymers, early termination reactions during polymerization, or oxidation. This is most pronounced for the amine-terminated poly(propylene oxide) polymer.

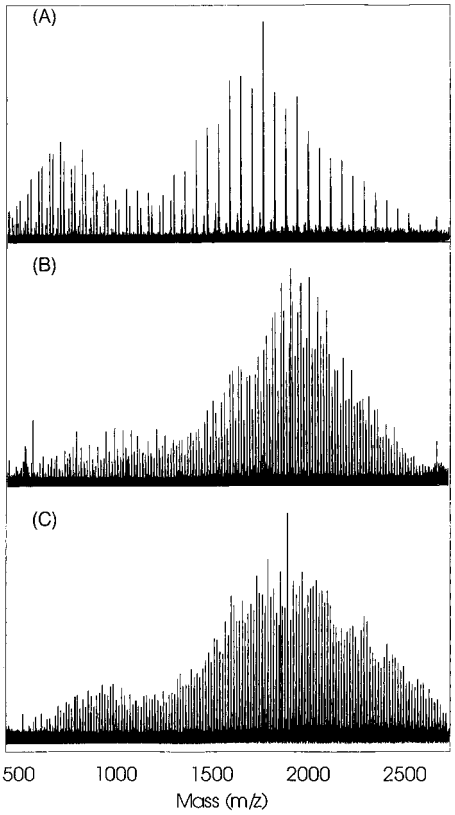


Figure 3. Molecular weight distributions of Jeffamine D-2000 (A), Jeffamine ED-2001 (B), and Jeffamine M-2070 (C) reconstructed by overlaying broad band MALDI FT-ICR-MS spectra obtained at systematically increased gated trapping times. These were respectively 500−2100 μs at 100 μs intervals (A), 600−1400 μs at 100 μs intervals (B), and 1000−1400 μs at 100 μs intervals (C).

Table 1. M_w, M_n, M_z, M_w/M_n, and M_p Values Calculated from Reconstructed Molecular Weight Distributions in Figure 3[a]

	Jeffamine D-2000	Jeffamine ED-2001	Jeffamine M-2070
M_n	1559	1716	1903
M_w	1746	1824	1996
M_z	1867	1908	2069
M_p	1779	1974	1904
M_w/M_n	1.12	1.06	1.05

[a] $M_n = \Sigma(N_iM_i)/\Sigma M_i$; $M_w = \Sigma(N_iM_i^2)/\Sigma(N_iM_i)$; $M_z = (N_iM_i^3)/\Sigma(N_iM_i^2)$; M_p = most probable (abundant) peak in the mass spectrum. In these formulas, N_i and M_i represent signal intensity and mass at point i.

From these spectra the number-average molecular weight (M_n), the weight-average molecular weight (M_w), the z-average molecular weight (M_z), the most probable molecular weight (M_p),[22] the and the polydisperity index (M_w/M_n) were calculated using the standard formulas. Results are listed in Table 1.

End Group Determination. Polyoxyalkeneamines consist of mixtures of oligomers with a variable degree of polymerization caused by the statistical nature of the polymerization process. This is reflected in the MALDI mass spectra by series of ions occurring at equidistant intervals of 44 Da for EO repeat units, 58 Da for PO repeat units, and 14 Da for EO/PO copolymers. The measured mass (M_{meas}) of individual molecules in the molecular weight distribution is described by a linear function ($M_{meas} = n \times M$(repeat unit) + M(end group) + M(cation)). Linear regression analysis is performed by plotting the measured masses of homologous ion series as a function of degree of polymerization (n). This yields the mass of the repeating unit (the slope) and the sum of the end group mass plus the mass of the cation (y-intercept, for $n = 0$). A criterion for assignment of n is that the estimated end group mass corresponds with organic functionalities which are plausible in the context of reaction mechanisms in polymer synthesis. In this respect, NMR analysis yields useful complementary information to FTMS data because the NMR data constrains the number of possible end groups and also yields information on the molar content of different monomers present in copolymers. Practical considerations and automatization of polymer mass spectra interpretation by linear regression algorithms have been discussed, recently.[31,32,37]

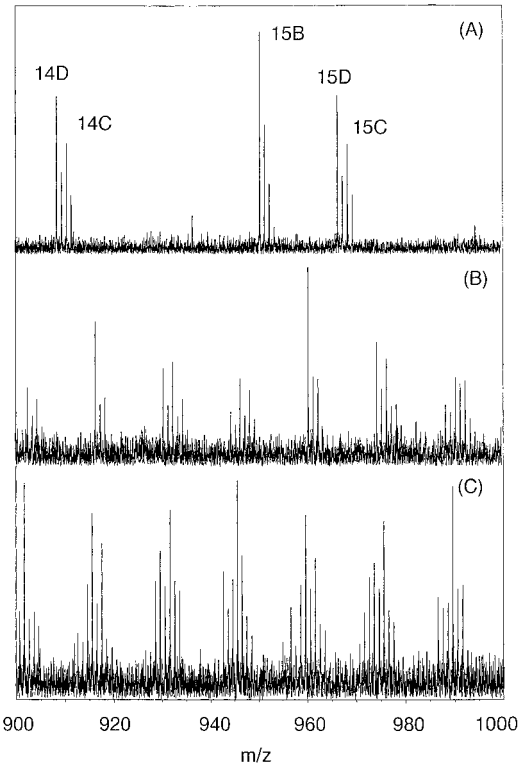


Figure 4. Enlargement of the broad band MALDI FT-ICR-MS spectra of Jeffamine D-2000 (A), Jeffamine ED-2001 (B), and Jeffamine M-2070 (C) (m/z range 900−1000). Labeled peaks in part A correspond to $[H_2N-(C_3H_6O)_n-C_3H_5 + Na]^+$ (15B, $n = 15$), $[H_2N-(C_3H_6O)_n-H + Na]^+$ (14C, $n = 15$; 15C, $n = 16$), and $[H_2N-(C_3H_6O)_n-C_3H_5O + Na]^+$ (14D, $n = 14$; 15D, $n = 15$).

All MALDI spectra are obtained in broad-band mode with a resolution $(m/\Delta m)_{50\%}$ of typically 30 000 around m/z 1500. Figures 4 and 5 show enlargements of the broad-band mass spectra of the three polyoxyalkyleneamines which illustrate that this resolution is more than sufficient to resolve the naturally occurring $^{12}C/^{13}C$ isotopes of the component molecules. Only sodium-adduct ions $[M + Na]^+$ are observed in the mass spectra. This was verified by spiking the samples with sodium, potassium, or lithium salts. In general, all components of the molecular weight distribution are measured with a mass accuracy better than 20 millimass units. This allows end group and repeat unit determinations with an accuracy within 50 millimass units for the molecular weight range from m/z 500 to 3500. The results of the end group and repeat unit determination by MALDI FT-ICR-MS are given in Table 2.

Regression analysis of the mass spectrum of the Jeffamine D-2000 diamine polyether shows that the

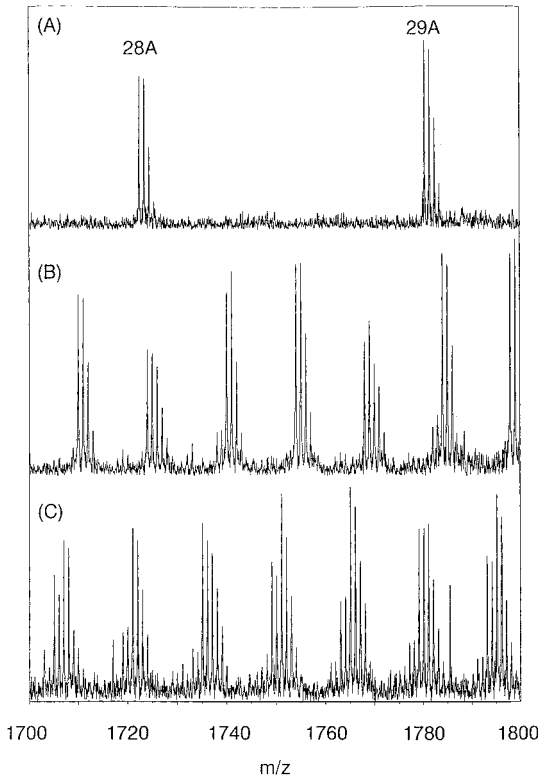


Figure 5. Enlargement of the broad-band MALDI FT-ICR-MS spectra of Jeffamine D-2000 (A), Jeffamine ED-2001 (B), and Jeffamine M-2070 (C) (m/z range 1700−1800). Labeled peaks in part A correspond to $[H_2N-(C_3H_6O)_n-C_3H_8N + Na]^+$ (28A, $n = 28$; 29A, $n = 29$).

dominant distribution in Figure 2A consist of amine-terminated polypropylene glycols of the type $[H_2N-(C_3H_6O)_n-C_3H_8N + Na]^+$, as specified by the manufacturer. The molecular weight distribution of this series exhibits a M_p of m/z 1606 ($n = 26$) and covers a mass range from m/z 1257 to 2128 ($n = 20-35$). The calculated repeat unit mass (58.0412 Da) is in good agreement with the exact mass of a PO monomer unit (58.0419 Da). In the mass spectrum also an ion series containing free hydroxyl end groups is observed with the structure $[H_2N-(C_3H_6O)_n-H + Na]^+$. These terminal hydroxyl groups result from incomplete reductive amination of the corresponding polyoxyalkylene polyols. The molecular weight distribution of this series is only completely resolved in the low molecular weight range of the spectrum from m/z 678 to 1258 (Figure 4). At higher molecular weights the resolution used in broad-band mode is not sufficient to resolve the mass difference between the naturally occurring ^{13}C isotope of the diamine polyethers and the monoisotopic ^{12}C peak of the monoamine polyethers with a free hydroxyl group. For example, the separation of the peak arising from the ^{13}C isotope of $[H_2N-(C_3H_6O)_n-C_3H_8N + Na]^+$ ($n = 23$, m/z 1433.0399) from the peak arising from the ^{12}C isotope of $[H_2N-(C_3H_6O)_n-H + Na]^+$ ($n = 24$, m/z 1433.0205) requires a minimum resolution $(m/\Delta m)_{50\%}$ of ∼75 000, which is only available in heterodyne mode. However, the presence of polyethers with free hydroxyl groups at high molecular weight is easily observed in broad-band measurements by the increase of the expected natural isotopic ratio for the diamine polyether series.

Two other prominent ion series are observed in the low molecular weight part of the mass spectrum from m/z 500 to 1500 (Figure 3A, enlargement shown in Figure 4a). Calculation of the residual end group mass by regression analysis of the homologous ion series observed from m/z 660 to 1531, with a M_p at m/z 950, yields 57.0628 (excluding the mass of the sodium cation), corresponding to the sum of C_3H_5 and NH_2 (Table 2). The occurrence of the unsaturated structure in polyethers is well-known and may result from dehydration of terminal hydroxyl groups during polymerization, leading to early termination. This would explain the relatively low M_p of m/z 950 of this homologous series. Another possible mechanism for the formation of allyl functionalities is the rearrangement of propylene oxide to an α,β-unsaturated allyl alcohol.[38,39] Regression analysis of the ion series observed from m/z 618 to 1489 with a M_p at m/z 908 yields an residual end group mass of 73.0592, which is in good agreement with the sum of the elemental composition of C_3H_5O and NH_2 (Table 2). This would point to the presence of ketone or aldehyde functionalities in the polymer probably as a result of oxidation processes. However, careful selection of experimental parameters is necessary for unequivocal assignment of the C_3H_5O and C_3H_5 end group structures in polyols, as Lattimer *et al.* showed that similar ion series could be produced as fragment ions during high-energy tandem mass spectrometric studies of poly(ethylene glycol) using fast-atom-bombardment (FAB) to produce the ions.[40,41] On the basis of the fact that these types of fragments were not observed in previous MALDI FT-ICR-MS studies on poly(ethylene glycol), using similar experimental conditions, we are confident that these end groups are actually present in the original polymer mixture.[31,32] Another possible end group combination is C_4H_9 (isobutyl alcohol or butyl alcohol initiator) and NH_2, corresponding to a mass of 73.0892. The C_4H_9 and C_3H_5O end groups have the same nominal mass of 57 with a mass difference of 36 millimass units which cannot be resolved in broad-band FT-ICR-MS analysis. In this study, the Jeffamine D-2000 sample was not analyzed by NMR and is merely used to illustrate that even for the characterization of relatively simple homopolymer systems complementary analytical information is highly desirable.

The mass spectra of Jeffamine ED-2001 and Jeffamine M-2070, shown in Figures 3−5, illustrate the increasing complexity of the chemical composition distribution of copolymers with respect to that of homopolymers. The major ion series in the mass spectrum of the Jeffamine ED-2001 copolymer is best described by $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_8N + Na]^+$. Several oligomeric series, with m ranging from 17 to 44 and n ranging from 0 to 4 are identified, demonstrating that this amine-terminated copolymer is mainly based on a EO backbone, as specified by the manufacturer. Repeat unit masses of 44.0267 and 58.0396 were calculated by plotting the measured mass as a function of the number of EO or PO repeat units, respectively (Table 2).

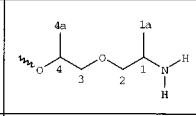
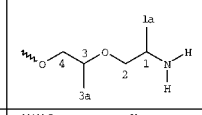
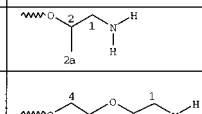
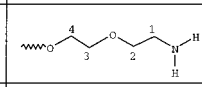
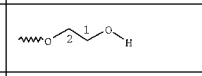
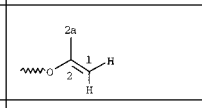
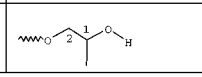
End groups in Jeffamine ED-2001 were identified using both ^1H and ^{13}C NMR. The relative contents of the identified end groups are summarized in Table 3. All ether-type protons overlapped in a very crowded region of the spectrum between 3.4 and 3.8 ppm. The protons of the ethylene oxide chain showed an intense singlet at 3.65 ppm. NMR data show the presence of predominantly primary amine end groups such as structures **A** and **B** (Table 3), demonstrating that Jeffamine ED-2001 consists of a polyethylene glycol end capped with propylene oxide. The 1-amino-1-methylethylene structures **A** and **B** showed double signals in

Table 2. Masses and Deviations in the Analysis of Jeffamines by MALDI FT-ICR-MS Obtained by Linear Regression Analysis[a]

	M_{calc}	M_{meas}	ΔM_{end}	$M_{mono,calc}$	$M_{mono,meas}$	ΔM_{mono}
		Jeffamine D-2000				
$H_2N-(C_3H_6O)_n-C_3H_8N$	74.0844	74.0914	−0.0070	58.0419	58.0412	−0.0007
$H_2N-(C_3H_6O)_n-H$	17.0265	17.0171	0.0095	58.0419	58.0425	0.0006
$H_2N-(C_3H_6O)_n-C_3H_5$	57.0579	57.0628	0.0050	58.0419	58.0415	−0.0004
$H_2N-(C_3H_6O)_n-C_3H_5O$[b]	73.0528	73.0592	0.0064	58.0419	58.0413	−0.0005
		Jeffamine ED-2001				
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_8N$	74.0844	74.0705	0.0139	44.0262	44.0267	0.0005
				58.0419	58.0396	0.0022
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-H$	17.0266	17.0277	−0.0012	44.0262	44.0270	−0.0008
				58.0419	*c*	
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-CH_3$	31.0422	31.0100	0.0322	44.0262	44.0275	−0.0013
				58.0419	58.0475	−0.0057
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_5$[d]	57.0579	57.0530	0.0049	44.0262	44.0274	−0.0012
				58.0419	58.0415	0.0004
		Jeffamine M-2070				
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-CH_3$	31.0422	31.0411	−0.0011	44.0262	44.0262	−0.0001
				58.0419	58.0417	0.0002
$HO-(C_2H_4O)_m(C_3H_6O)_n-CH_3$	32.0262	*e*				
$H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_8N$	74.0844	74.0506	0.0338	44.0262	44.0252	0.0010
				58.0419	58.0408	0.0010
$CH_3O-(C_2H_4O)_m(C_3H_6O)_n-C_3H_5$[f]	72.0575	72.0513	0.0062	44.0262	44.0267	−0.0005
				58.0419	58.0415	0.0004

[a] The mass deviations in the end group mass (ΔM_{end}) are defined as the difference between the actual end group mass (M_{calc}) and the measured mass (M_{meas}). The mass deviations in the repeat unit mass (ΔM_{mono}) are defined as the difference between the actual end group mass ($M_{mono,calc}$) and the measured mass ($M_{mono,meas}$). [b] This series overlaps with $H_2N-(C_3H_6O)_n-C_4H_9$. [c] Not enough data points for regression analysis. [d] This ion series overlaps with $H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_5O$. [e] Present but not resolved. [f] This ion series overlaps with $CH_3O(C_2H_4O)_m(C_3H_6O)_n-C_3H_5O$.

Table 3. NMR Data of Jeffamines

end group	Structure	ED-2001 abundance (Mol%)	M-2070 abundance (Mol%)	C shift (ppm)	H shift (ppm)
A		2.8	0.5	1 48.8;48.1 1a 15 2 76 3 73 4 77 4a 17	3.18 1.04 3.4-3.8 3.4-3.8 3.4-3.8 1.15
B		0.7	1.1	1 50.1;47.8 1a 15 2 75.5 3 76 3a 17 4 72.5	3.1 1.04 3.4-3.8 3.4-3.8 1.15 3.4-3.8
C		<< 0.1	<< 0.1	1 55 2 - 2a -	- - -
D		0.3	< 0.1	1 40 2 68.5	2.9 -
E		0.25	< 0.1	1 61	-
F		< 0.1	<< 0.1	1 76 2 161 2a 16	- -
G		0.25	2.2	1 59	3.38
H		< 0.2	< 0.1	1 68.3	-

the NMR data because of diastereoisomerism. The presence of a fraction of ethyleneamines, resulting from amination of terminal hydroxyl groups on ethylene units, is illustrated by structure **D** in Table 3. These NMR data are in good agreement with NMR data on Jeffamine ED-800.[42] End group structures **C**, **E**, **F**, and **H** were not visible in the ^1H spectrum of Jeffamine ED-2001 due to signal overlap. However they were detected in the ^{13}C spectrum of a highly concentrated solution (in chloroform-*d*), obtained in a weekend run.

In the FT-ICR-MS spectrum of the Jeffamine ED-2001 copolymer, a series of compounds with free hydroxyl groups are detected which are described by $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-H + Na]^+$. ^{13}C NMR analysis reveals that the abundance of unreacted hydroxyl groups on terminal ethylene units (Table 3, structure **E**) predominates over unreacted hydroxyl groups on terminal propylene units (structure H). This demonstrates that secondary hydroxyl groups of the polyoxyalkylene are more susceptible toward reductive amination that primary hydroxyl groups. In the FT-ICR-MS data, several homologous series are observed with $\Delta m/z$ 16 ranging from m/z 652 to 1546 which fit with the structural formula $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-CH_3 + Na]^+$. Regression analysis of these ion series yields a residual end group mass of 31.0100 corresponding to CH_3 and NH_2. The presence of a relatively high abundance of OCH_3 end groups in the NMR data (structure **G**, Table 3) confirms this identification. Taking into account that, for the main oligomeric series $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_8N + Na]^+$, m ranges from 17 to 44 and n ranges only from 0 to 4, a much lower m/n (EO/PO) ratio is required to fit the $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-CH_3 + Na]^+$ series on the low molecular weight distribution. Therefore, we conclude that this Jeffamine ED-2001 sample is contaminated, most likely with a Jeffamine M-1000 monoamine.

However, care should be taken when interpreting the oligomeric series in the low molecular weight fraction in Jeffamine ED-2001 using only the FT-ICR-MS data. If we use another EO/PO ratio as input for the regression analysis, we obtain end group masses of 57.0530 and 73.05310, corresponding to $[H_2N-(C_2H_4O)_m-(C_3H_6O)_n-C_3H_5 + Na]^+$ and $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_5O + Na]^+$, respectively. Another factor to consider, when interpreting these oligomeric series in the FT-ICR-MS data, is that the mass difference between 3 EO units ($C_6H_{12}O_3$) and 2 PO units ($C_6H_{12}O_2$) equals 1 oxygen atom ($\Delta m/z$ 16). Consequently, $[H_2N-(C_2H_4O)_n-(C_3H_6O)_m-C_3H_5 + Na]^+$ and $[H_2N-(C_2H_4O)_{n-3}-(C_3H_6O)_{n+2}-C_3H_5O + Na]^+$ yield exactly the same elemental composition. ^{13}C NMR data, listed in Table

3, confirm the presence of unsaturated allyl functionalities in the polymer, but aldehyde, ketone, or OC(CH_3)=CHOH functionalities were not detected by NMR (detection limit < 0.02 Mol %). Since the MALDI ionization efficiencies of Jeffamines containing various end groups in the polymer mixture are unknown, it is not possible to make a quantitative comparison between the FT-ICR-MS and NMR data, yet.

The major ion series in the mass spectrum of the Jeffamine M-2070 monoamine copolymer corresponds with the general formula $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-CH_3 + Na]^+$. This confirms that this monoamine copolymer is prepared by reaction of a methanol initiator with EO and PO followed by amination of the terminal hydroxyl group, as specified by the manufacturer. Several oligomer series, with *m* ranging from 14 to 46 and *n* ranging from 5 to 10, are identified. NMR analysis reveals that the end groups consist almost entirely of 1-amino-1-methylene (structures **A** and **B**, Table 3) and OCH_3 (structure **G**). The abundance of ethyleneamines (structure **D**) is low, indicating that this copolymer consists mainly of a poly(ethylene glycol) end capped with propylene oxide. The high abundance of OCH_3 terminal functional groups detected with NMR confirms that the main oligomeric series in this polymer are monoamines. A small fraction of hydroxyl end groups is observed with NMR (structures **E** and **H**, Table 3). In the broad-band mass spectra the peaks of the $[HO-(C_2H_4O)_m(C_3H_6O)_n-CH_3 + Na]^+$ oligomer series overlap with the peaks of the naturally occurring ^{13}C isotope of the major ion series of the copolyether monoamine. Consequently, the presence of hydroxyl end groups is only concluded from the increased abundance of the ^{13}C isotope signal of the monoamine.

In the low molecular weight part of the spectrum, a homologous series is observed between m/z 711 and 1043 with $\Delta m/z = 14$ Da and $M_p = 901$. Regression analysis yields an end group mass of 74.0506. Therefore, this ion series fits with the general formula of Jeffamine ED, *i.e.* $[H_2N-(C_2H_4O)_m(C_3H_6O)_n-C_3H_8N + Na]^+$, in which *m* varies between 7 and 16 and *n* varies between 1 and 6. However, if another EO/PO ratio is used as input for the regression analysis, a residual end group mass of 72.0513 is obtained, corresponding to a elemental composition of C_4H_8O. Therefore, this oligomer series can be completely described by $[CH_3O-(C_2H_4O)_m(C_3H_6O)_n-C_3H_5 + Na]^+$ (or $[CH_3O-(C_2H_4O)_m-(C_3H_6O)_n-C_3H_5O + Na]^+$, taking into account the mass difference of 16 Da between 3 EO and 2 PO units). (This gives an end group mass of 88.05415.) NMR shows no evidence for the presence of C_3H_5 (detection limit approximately 0.01 mol %). Also, no definite proof is obtained with ^{13}C NMR for the C_3H_5O end group, although a resonance observed at 103.4 ppm may arise from an OC(CH_3)=CHOH structure. In addition, more resonances were found in the ^{13}C NMR spectrum to which no definite structures could be assigned, yet (*e.g.* at 37.1 ppm). The combined FT-ICR-MS and NMR results lead to the conclusion that the low molecular weight polymer distribution mainly arises from a contamination, most likely Jeffamine ED (*e.g.* ED-900).

Conclusion

MALDI FT-ICR-MS analysis of polyoxyalkyleneamines allows rapid and accurate identification of the principal oligomer series with respect to molecular weight distribution, EO/PO distribution, and residual end group distribution. The repeat units and major end groups of monoamine and diamine polymers calculated by regression analysis of the mass spectral data are confirmed by NMR data.

In addition, several oligomer distributions are observed arising from contaminations, rearrangements, oxidation, and incomplete termination reactions. Identification of these structures is particularly interesting because they may cause performance differences between different batches of polyoxyalkylene amines. Various feasible residual end group combinations could be postulated by regression analysis of the mass spectra, but unambiguous identification of these polymers by FT-ICR-MS is prevented by the large number of possible structural permutations, which result in isomeric structures of the same elemental composition. Another complicating factor is the theoretical possibility of isobaric structures which are not resolved by FT-ICR-MS using a resolution of 30 000 in the m/z range from m/z 500 to 3500, during broad-band measurements. Complementary NMR data proved to be crucial to distinguish between these structural alternatives.

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