Direct Mass Spectrometric Analysis of Phenol–Formaldehyde Oligocondensates: A Comparative Desorption Ionization Study

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ABSTRACT: The characterization of oligomeric reaction products obtained by acid- or base-catalyzed condensation of phenol and formaldehyde is reported using desorption methods of ionization. Desorption electron ionization (DEI) and chemical ionization (DCI), thermospray (TSP), potassium ionization of desorbed species (K⁺IDS), field desorption (FD), and fast atom bombardment (FAB) techniques were performed on commercial sector or quadrupole instruments. The recorded mass spectra are interpreted in terms of the prevailing mechanism of ionization, of possible thermal damage of the samples during analysis, and of furnishing quantitative data. The methods afford meaningful spectra of oligomers synthesized by acid-catalyzed condensation (Novolak), but reliable quantitative measures of molecular weight distribution are obtainable only from FD, K⁺IDS, and DEI mass spectra. Only FD is applicable directly to the base-catalyzed condensation products (resol-type resin), but acetylation allows useful FD and K⁺IDS spectra. The molecular weight averages for the resol-type resin is, however, accurate exclusively when they are computed from the FD mass spectrum of the derivatized sample.

Introduction

The statistical nature of the polymerization process generally affords polymeric/oligomeric materials that are composed of mixtures of molecules with a range of molecular weights. The determination of molecular weight distributions and the corresponding mathematical moments are important in the characterization of polymeric materials. For copolymers and terpolymers, there is, in addition to the molecular weight distribution, a chemical composition distribution (CDD) which must also be determined to fully characterize these materials and understand their properties. A number of established and new techniques have the capability of furnishing compositional and/or molecular weight information.[1]

Mass spectrometry is an emerging technique in this field[2-4] and has some rather unique advantages. Individual molecules can be directly examined, thus qualitative information (compound identification) and quantitative data can be furnished by a variety of methods based on mass spectrometry. Direct analysis of oligomers/polymers requires no or minimal sample preparation, and the analysis usually takes only minutes. A spectrum of molecular and fragment ions can reveal the chemical composition of the polymer. Mass and intensity data may be used for the characterization of molecular weight distribution and for calculation of the average molecular weights. In practice, the most common quantitative measures of the molecular weight distribution are obtained as follows:

$$M_n = \sum N_i M_i / \sum N_i$$
number-average molecular weight (1)

$$M_w = \sum N_i M_i^2 / \sum N_i M_i$$
weight-average molecular weight (2)

$$Q = M_w / M_n \quad \text{polydispersity} \quad (3)$$

N_i may be directly substituted with the I_i intensity for the species with molecular mass M_i. It is known that copol-

ymer properties are affected by the monomer sequence (random, block, etc. copolymers) in addition to the molecular weight, and most copolymers also have a chemical composition distribution.[5]

"Soft" ionization eliminating or reducing the subsequent formation of fragment ions (due to surplus internal energy transferred to the molecular ion during ionization) in the ion source is usually preferred for direct polymer analysis due to the polydisperse character of these substances. Intense fragment ions such as those observed in electron ionization (EI) mass spectra may obscure intact molecular ions, and the extent of fragmentation may vary with the molecular weight; thus precluding the calculation of reliable molecular weight data. The principal difficulty with techniques employing vaporization prior to ionization in the mass spectrometer, but otherwise fulfilling the criterion of soft ionization (e.g., chemical ionization or field ionization), is the nonvolatility of polymers. Thermal decomposition during this type of sample introduction is commonplace. This is why desorption methods of ionization, which produce intact gaseous ions directly from the condensed (solid or liquid) phase samples, have received attention.

The desorption ionization (DI) techniques are, however, different in terms of the principles of ion generation. Several methods apply rapid heating, that favors desorption of intact molecules over thermal decomposition, and ionization of these desorbed species in the proximity of the vaporization ("in-beam" techniques).[6] Desorption directly from the liquid (solution) or solid phase may be induced by an external electric field (field desorption[7]) or by a high electric field emerging from charged liquid droplets as the solvent is removed (electrospray ionization[8]). Bombardment with energetic particles (fast atom bombardment,[9] secondary-ion mass spectrometry[10]) and laser irradiation (laser desorption[11,12]) are also commonly used techniques that result in the desorption of analyte molecules. The interplay between the sample characteristics and the principle(s) of ion generation will ultimately affect the success of direct analysis for a particular class of oligomers. Nevertheless, impressive results have been

obtained by DI techniques for a number of low molecular weight polymers, and the quantitative data have shown agreement with those determined by methods other than mass spectrometry such as vapor pressure osmometry, gel permeation chromatography, and end-group analysis.[13,14] Most of the studies have concentrated on the sole application of a particular method of ionization/desorption. With routine instrumentation (sector and quadrupole instruments), FD and FAB methods have enjoyed widespread use for polymer applications. Numerous publications by Lattimer et al.[13,15,16] and Saito et al.[17–19] have revealed the utility of FD in this field. Montaudo and co-workers have excelled in application of FAB mass spectrometry to the characterization of synthetic oligomers/polymers.[20,21] However, comparative evaluations of the relative merits and pitfalls of alternative (or complementary) DI techniques with respect of given oligomeric/polymeric substances have been scarce. (Review papers[2–4,22] have addressed this issue, but the conclusions were based on literature references rather than systematic studies.)

The initiative for comparative studies of phenol–formaldehyde condensates (resins) with DI techniques has been the need for reliable means of compositional characterization and of molecular weight distribution determination. Nuclear magnetic resonance (NMR) spectrometry has been a suitable method for compositional characterization and furnishing number-average molecular weight data,[23] but information on molecular weight distribution is not attainable. Gel permeation chromatography may suffer from the aggregation of the phenol–formaldehyde oligomer molecules, making qualitative and quantitative determination unreliable.[24] Gas chromatography,[25–28] supercritical fluid chromatography,[29] and high-performance liquid chromatography[30–32] have revealed important details on individual oligomer species, but quantitative measures of the molecular weight distribution could not be obtained due to the limited depth of analyses. Field desorption (FD) mass spectrometry has, however, produced promising results[33–35] that could be fully exploited for the characterization of phenol–formaldehyde resins.

In this paper, we report a comparative desorption ionization study for the oligomeric reaction products obtained by acid- and base-catalyzed condensation of phenol and formaldehyde. The methods we selected were desorption or "in-beam" electron ionization (DEI) and chemical ionization (DCI), thermospray (TSP), potassium ionization of desorbed species (K⁺IDS), field desorption, and fast atom bombardment (FAB). All of these ionization methods were performed on commercial quadrupole or sector instruments. The obtained DI mass spectra are interpreted in terms of the expected intact species (molecular or adduct ions) and the prevailing mechanism of ionization under the applied experimental conditions. Assignment of fragments and/or decomposition reaction (pyrolysis), if any, is considered an important issue. These may affect the accuracy of quantitative measures of molecular weight distribution.

Experimental Section

The samples involved in this study were obtained by the acid- or base-catalyzed condensation of phenol and formaldehyde, as previously described.[25,26] The prepolymers obtained by acid catalysis with a molar excess of phenol are commonly called Novolak-type resin. The base-catalyzed condensation products are the resol resins and are generally prepared in the presence of excess formaldehyde. Both resins were analyzed following acetylation by ¹H NMR spectrometry[23] using a GE-300 instrument (General Electric, Schenectady, NY) operating at 300-MHz

resonance frequency. The measurements were carried out in triplicate, and the calculated number-average molecular weight (M_n) was reported with the standard deviation.

DEI and FD mass spectra were recorded on a JMS-01SG-2 double-focusing instrument (JEOL, Tokyo, Japan) operated at a resolution of better than 1000 (from the width of a single peak at 5 % height). Mass spectra were acquired by a JMA-2000 data system in the range m/z 20 to 800 at a scan rate of 5 s/decade. This mass range was calibrated with perfluorokerosene standard. The samples for DEI analysis were placed onto the surface of a 80-μm-o.d. tungsten wire which was subsequently introduced into the mass spectrometer's standard EI source. Vaporization was achieved by direct electrical heating via the sample heating circuit of the source, and the current was switched to the maximum value (ca. 1.5 A) immediately after the introduction of the wire. The energy of the ionizing electrons was 14 eV, a beam current of 100 μA was maintained in the source, and the accelerating voltage was 10 kV.

FD spectra were obtained by a combined FD/FI/EI source. Tungsten wires of 10-μm o.d. (spotwelded onto a standard holder consisting of two metal rods 5 mm apart) activated at high temperature with benzonitrile were used as emitters.[36] The samples were coated onto the surface of the emitter from acetone solutions by the syringe loading technique.[37] No source heating was applied during the analyses. The counter electrode (cathode) and the emitter were held at −3 and 10 kV, respectively. Desorption was induced by raising the emitter heating current gradually from 0 to 35 mA, but only the spectra obtained from 10 to 30 mA were averaged. Mass-scale calibration was established in the EI mode using perfluorokerosene (20–800 Da mass range).

The TSP instrument was a quadrupole-based system (Model 200, Vestec, Houston, TX). The TSP solution (0.1 M aqueous NH₄OAc/acetonitrile, 7/3) was introduced at a 1.0 mL/min flow rate (by a Kratos Spectroflow 430 solvent delivery system) via a stainless steel capillary (¹/₁₆-in. o.d × 0.006-in. i.d.) inserted into the mass spectrometer. Vaporization was accomplished by direct electrical heating of the capillary. The following TSP conditions were applied: control temperature 145 °C; vaporizer 220 °C; source 300 °C; tip heater 325 °C. The thoriated iridium filament was operated at 1000-V and 100-μA total emission. The sample was dissolved in the TSP solution, and introduction was made by a Rheodyne Model 7125 injector valve equipped with a 20-μL loop (Cotati, CA). The spectrometer was scanned from m/z 80 to 1000 (full scan 2.8 s). Mass-scale calibration was achieved by poly(ethylene glycol) oligomers as standards (thermospray ionization in 0.1 M NH₄OAc buffer, filament off). Quadrupole mass spectrometers are susceptible to emphasize low- or high-mass ions, depending on the instrumental conditions. The accuracy of the molecular weight data calculated from TSP mass spectra were evaluated by analyzing commercially available poly(ethylene glycol) (PEG) oligomer mixtures (Aldrich, Milwaukee, WI). The number-average molecular weight of PEG 400 was determined to be 430 (Δ = +7.5 % relative error from the value specified by the supplier), and the PEG 1000 standard yielded M_n = 960 (Δ = −4 %). However, a slightly different quadrupole setting was necessary to achieve the specified accuracy for the higher molecular weight poly(ethylene glycol) mixture. In our experiments, the parameters adjusted to PEG 400 were used.

DCI and K⁺IDS mass spectra were recorded on a Model 4615B quadrupole GC/MS system (Finnigan MAT, San Jose, CA). The mass spectrometer was tuned and calibrated with tris(perfluoroheptyl)-(S)-triazine (PCR, Gainesville, FL) which possesses significant ions up to 1185 daltons (Da). The tuning parameters were adjusted to enhance the transmission of high-mass ions (>500 Da). Mass spectra were recorded at nominal resolution of 1500 at 1000 Da/s speed. Three to five scans were averaged to obtain reproducible mass spectra. Methane was used as the CI reagent gas. The ion source pressure (measured by a Pirani gauge) was 0.5 Torr with a source temperature of 200 °C. The samples were coated from acetone or methanol solutions onto the rhenium wire (0.004-in. diameter, supplied by Scientific Instrument Services, Ringoes, NJ) of the DCI probe. The wire current was raised to 1.35 A at ca. 1 A/s during the analysis, thus providing the maximum ramp rate attainable by the programmable DCI power supply.

An EI source configuration was used in the K⁺IDS experiments on the quadrupole instrument. The ion source pressure (ion gauge) was less than 10^{-6} Torr with a source temperature of 200 °C. Thermionic K⁺-containing glass ($1 K_2O:1 Al_2O_3:2 SiO_2$), which was prepared as described earlier,[38] was applied to the direct-exposure probe rhenium filaments (0.004-in. o.d.). Potassium ion emission was induced by heating the wire to in excess of 1000 °C. The samples were deposited on a stainless-steel ribbon (0.001 in. × 0.125 in., Scientific Instrument Services, Ringoes, NJ) placed 0.5 mm above the emitter filament. For a more detailed description of the K⁺IDS setup, consult ref 38. To evaluate the accuracy of the molecular weight data afforded by K⁺IDS, we applied poly(ethylene oxide) standards, PEO 300 and PEO 1200 (Scientific Polymer Products, Inc., Ontario, NY). The calculated molecular weight averages for the 300 and 1200 poly(ethylene oxide) were 292 (relative error $\Delta = -2.7\%$) and 1120 ($\Delta = -6.7\%$), respectively.[39]

Alternative DCI mass spectra were obtained with an MS80RFA double-focusing instrument (Kratos Analytical, Manchester, U.K.). The samples (0.1–1.0 μg) were supplied onto the platinum–iridium coil of the DCI probe using acetone as a solvent which was allowed to evaporate at room temperature. The probe was inserted into the combined EI/CI source. The following conditions were applied: reagent gas, isobutane (99.5+%); electron energy, 50 eV; emission current, 500 μA; source temperature, 50 °C; source pressure, ca. 10^{-5} Torr (source vacuum gauge). Positive ion spectra were recorded at 4.0-kV accelerating voltage in the mass range 50–800 Da (calibrated with perfluorokerosene in the EI mode). The nominal resolution was 1000. The mass spectrometer was scanned at a rate of 1 s/decade, while the sample coil was directly heated from 50 to 600 °C at 100 °C/s and then held at the final temperature for 20 s.

FAB mass spectra were registered with the MS80RFA instrument operated at 4.0-kV acceleration voltage, 1500 nominal resolution, and a scan rate of 10 s/decade. The FAB gun was a saddle-field source (FAB11NF, Ion Tech Ltd., Teddington, Middlesex, U.K.) supplied with xenon gas (99.995%) and producing fast atoms/ions at 8-keV energy and 1-mA current. Sample introduction was accomplished by dissolving 100–500 μg of material in 1–2 μL of liquid matrix placed on the copper tip of the FAB target. The matrix was either glycerol-containing sodium chloride (1 M/L) or 3-nitrobenzyl alcohol. Mass spectra were collected from 80 to 1500 Da, mass-scale calibration was established with the FAB ionization (without matrix) of a cesium iodide/rubidium iodide (1:1 molar ratio) salt mixture.

Several runs (at least five) were averaged for each DI analysis to assure the precision and repeatability of measurements. Calculation of molecular weight averages and polydispersity were performed off-line (LOTUS 1-2-3 spreadsheet software[40]).

Results and Discussion

Novolak-Type Resin. The prepolymer obtained by the acid-catalyzed condensation represents oligomeric species with the general formula as given in I. The

(I)
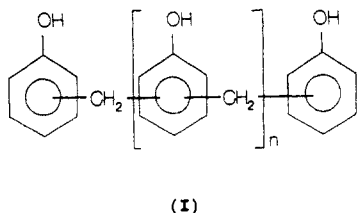
condensation in aqueous media practically precludes the formation of products with a high degree of condensation, mainly due to the decreasing solubility of the latter in the reaction mixture, and the relative molecular weight of these thermally stable oligomers remain normally below 1000 Da.

All of the DI techniques involved in the study afforded meaningful spectra. DEI using low-energy ionizing electrons (Figure 1) results in a series of high-intensity molecular ions (M·⁺) with a spacing of 106 Da. Fragmentation of the above odd-electron ions is minimal. There
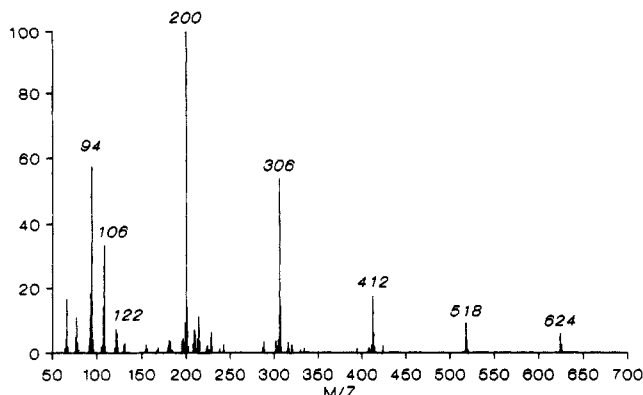

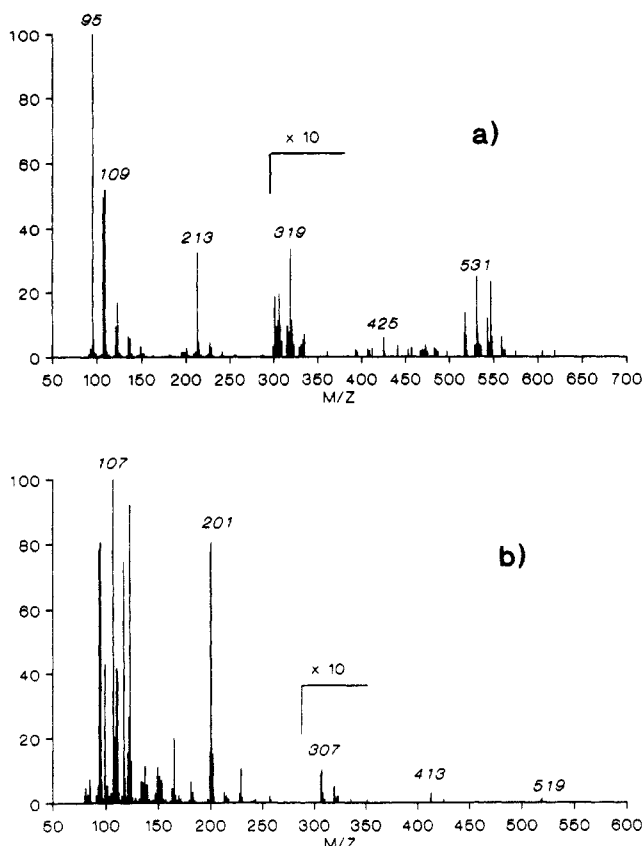**Figure 1.** DEI mass spectrum (14 eV) of the Novolak-type phenol–formaldehyde resin.

Figure 2. DCI mass spectra of the Novolak-type resin: (a) methane reagent gas, quadrupole instrument; (b) isobutane reagent gas, sector instrument.

are, however, additional "satellite" peaks accompanying the phenol (m/z 94) and the lower-mass oligomers in 14-Da increments. It has been shown that thermal decomposition of higher molecular weight oligomers of I results in methyl-substituted phenols[41] such as cresols (M·⁺ at m/z 108) and xylenols (m/z 122), and methyl-substituted polynuclear phenols (m/z 214, 228, etc.) can also be expected from this reaction.[42] The presence of the corresponding peaks is an indication of pyrolysis reactions during sample introduction.

DCI (Figure 2) seems to be most affected by processes that obscure molecular weight information. Although the presence of the expected [M + H]⁺ ions (m/z 95, 201, 307, 412, etc.) can be identified, excessive fragmentation is observed (m/z 107, 213, 319), and pyrolysis products can also be identified. We have been unable to obtain sufficient improvement in the quality of the DCI mass spectra by adjusting the variables that may effect sample introduction and ionization in DCI, such as reagent gas, ramp rate, source temperature, sample amount, etc. (Note that there
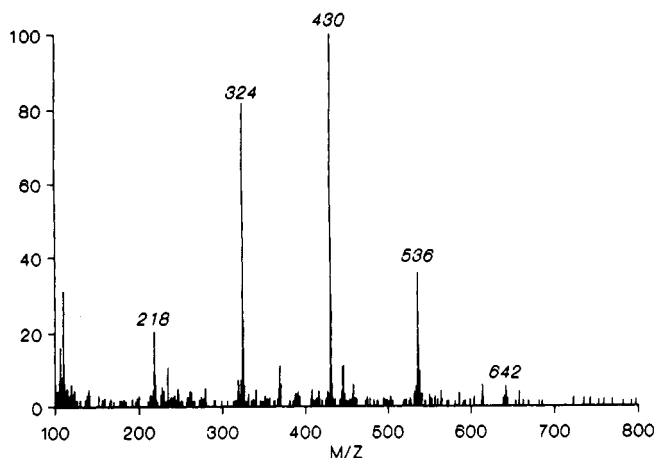
Figure 3. Thermospray ionization mass spectrum of the Novolak-type resin.

Figure 4. K⁺IDS mass spectrum of the Novolak-type resin.

Figure 5. FD mass spectrum of the Novolak-type resin.

are dissimilarities in spectra obtained by the quadrupole or the sector instrument which may be due to the different probe construction and also to changing the reagent gas from methane to isobutane.) This phenomenon is not well understood. A possible reason for thermal decomposition might include the existence of a large temperature gradient within the sample layer deposited onto the surface of the wire. Thus, the molecules at the metal wire/sample boundary may be pyrolyzed prior to vaporization. Fragmentation in the gas phase can also be originated in the energetics of proton transfer from the reagent ions to the analyte molecules. Exothermic reactions may result in surplus internal energy incorporated in the protonated molecule, thus leading to fragmentation. It appears that the cleavage of the benzylic bonds in the oligomer molecules is favored, giving rise to the m/z 107, 213, 319, 425, 531 ion series. This explanation is plausible, since these ions are more intense when methane was used for the registration of the DCI mass spectra. The proton transfer in this reagent gas system results in higher (exothermic) enthalpy change, as compared to that of isobutane.

We observed only weak [M + NH₄]⁺ ions using *thermospray ionization*[43] (by the ammonium acetate buffer only). Better results have been obtained when the thermospray is used as a means for sample *vaporization*, and the ionization is effected by an external technique such as via an electron-emitting filament. The electrons first create a reagent plasma (containing protonated molecules, ammonium adducts) from the solvent, and the vaporized sample molecules are ionized through a CI-like process. (Clearly, ionization occurs in the gas phase here, and classification of this method as being desorption ionization is justified only in terms of the proximity of the ionization and the flash sample vaporization from the droplets.) Figure 3 shows the filament-on TSP mass spectrum of Novolak obtained by introducing the sample in 0.1 M NH₄OAc/acetonitrile (7/3) solution. The appearance of the [M + NH₄]⁺ ions of the oligomer species (m/z 218, 324, 430, 536, 642) indicates that the mechanism of ionization is similar to that operating under ammonia CI conditions. In contrast with DCI, thermal decomposition accompanying sample introduction is minimal.

K⁺IDS also furnishes quasi-molecular ions in the form of [M + K]⁺ adducts (m/z 133, 239, 345, etc.), as shown in Figure 4. Owing to the implementation of the two-filament design,[44] minimal thermal decomposition of the sample is expected. Indeed, this unwanted chemical reaction occurring prior to ionization was negligible for the Novolak-type resin. The presence of ions, albeit with low intensity, at m/z 200, 306, and 412 is noteworthy. This may be due to surface ionization, and the potassium ions
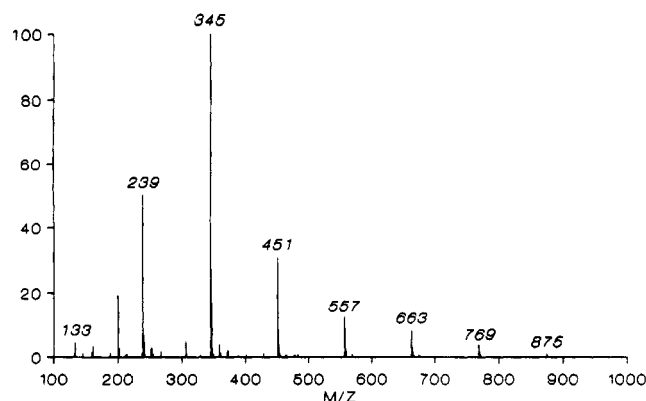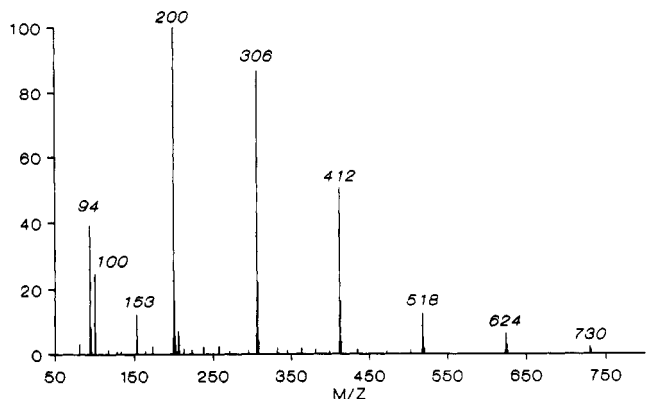
impinging against the surface of the sample might also expel odd-electron molecular ions.

FD provides exclusively molecular ions (Figure 5). Besides the odd-electron M⁺ species (m/z 94, 200, 306, 412, ..., up to the heptamer m/z 730) which represent the majority of the total ion current, doubly-charged M²⁺ ions of the dimer, trimer, and tetramer are also discernible at m/z 100, 153, and 206. This is an indication, that electron tunneling at high electric field (>10⁻⁹ V m⁻¹) is the dominating mechanism of ionization.[45] It is observed by the stereomicroscope used for sample deposition that the majority of the resin was deposited at the shanks of the field-enhancing microneedles of the activated emitter, which represent a low-field area. Surface diffusion can be excluded as a primary sample supply mechanism for the moderately polar Novolak oligomers, thus gas-phase transport must take place from the sample reservoirs to the tip of the microneedles where the analyte molecules become ionized in the gas phase,[46] i.e. by *field ionization* (FI). However, the distance from the site of sample deposition to that of ionization is minimal (10–20 μm on the average, a rough estimation from the length of the field-enhancing microneedles), and gas-phase transport over such a short distance and under the reduced pressure prevailing in the ion source at the proximity of the emitter is not accompanied by detectable thermal decomposition. The presence of the doubly-charged ions, another manifestation of the ionization occurring in the gas phase, can be attributed to the FI of field-adsorbed ions.[47]

A suitable liquid matrix in FAB ionization is a prerequisite. We have carried out experiments with several matrices reported in the literature.[48] In general, when the Novolak-type resin was dissolved in a neat, polar matrix such as glycerol, no analyte ions were produced upon bombardment with 6–8-keV xenon beam. When the matrix is doped with sodium chloride (Figure 6a), the FAB spectrum has shown several cation adducts ([M + Na]⁺) from high-mass oligomer molecules. We observed ions up
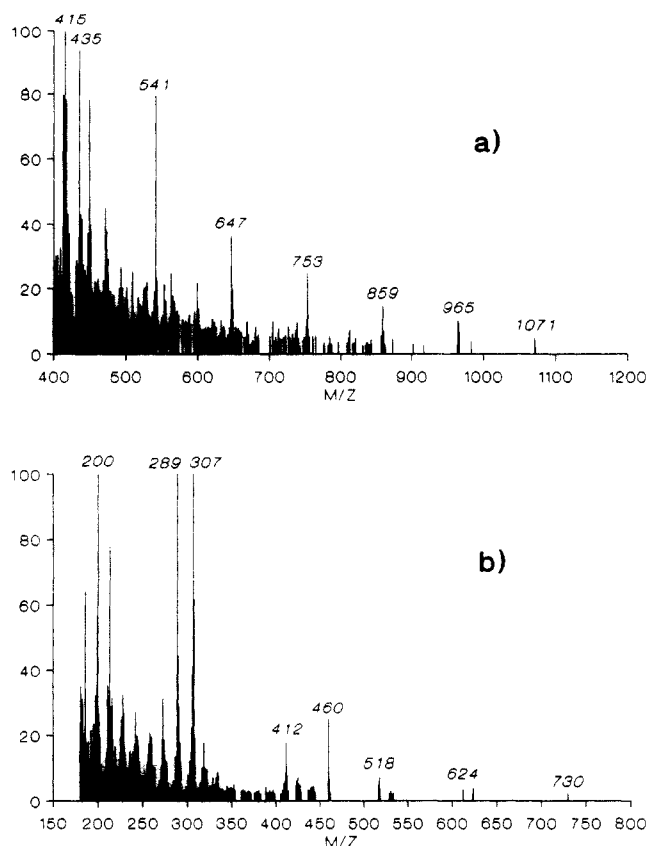
Figure 6. FAB mass spectra of the Novolak-type resin: (a) with glycerol matrix doped with sodium chloride; (b) with 3-nitrobenzyl alcohol matrix.

to the "sodiated" decamer (m/z 1071). Unfortunately, due to interference from matrix-related ions, oligomers below m/z 400 cannot be easily identified from the spectrum, although they probably exist. The low yield of desorbed species from the analyte as compared to that of the matrix is not surprising, since polynuclear phenols are less polar than most of the common FAB matrices.

Odd-electron molecular ions ($M^{\cdot +}$) are obtained from the sample dissolved in 3-nitrobenzyl alcohol and subjected to the energetic neutral beam, as shown in Figure 6b. Interestingly, the presence of considerable amount of alkali-metal salt in the matrix solution does not suppress the predominant formation of molecular ions, although cation adducts of the oligomer molecules are also seen. The interference from matrix ions is still a serious drawback that may preclude the identification of certain Novolak oligomers.

In summary, DI spectra of Novolak-type resins obtained during this study reflect that ionization occurs predominantly in the gas phase. It is obvious that vaporization of the sample must be involved in DEI, DCI, TSP, and K^+IDS, which is followed by the production of ions from the molecules present in the gas phase. This happens according to the principles peculiar to the particular method of ionization. The electron beam, the reagent-ion plasma, and the thermionic potassium ions are the means of generating positive ions, respectively. We also noted that under FD conditions the sample molecules also evaporated from the site of deposition to reach the tip of the field-enhancing microneedles where they become ionized from the gas phase by an FI mechanism resulting in mostly the odd-electron molecular ions. It is, however, somewhat difficult to interpret the sequence of events and the actual process of ionization under FAB conditions, although the formation of molecular ions seems to be an evidence for ionization in the gas phase.[49] Processes occurring in the selvedge region and similar to those

observed under charge-transfer ionization conditions should be in operation. Although the presence of the cation adducts using alkali-metal salt-doped matrix might be an indication of the direct desorption of preformed ions, it is believed that in the present case cation attachment takes place possibly in the gas phase, in or close to the selvedge region.[50]

Upon calculating average molecular weights (M_n and M_w) and polydispersity data (Q) from DI spectra, we undertook two approaches. The basis of the evaluation of the accuracy is the number-average molecular weight obtained from ^{1}H NMR spectrometric analysis, $M_n = 279 \pm 10$. We could not reliably estimate values from DCI and FAB mass spectra due difficulties described above. At first, the quantitative measures of the molecular weight distribution were calculated from the raw m/z versus intensity data. It has been realized that fragment ions and the molecular ions of pyrolysis products in DEI, the isotope pattern of potassium in K^+IDS, and the presence of double-charged molecular ions in FD may adversely influence the accuracy of the data obtained. In calculating the corrected values, only the ion intensities corresponding to the most abundant isotopic peak in the envelope of molecular or quasi-molecular ions of the oligomer series were used. Correction factors were calculated on the basis of the isotopic distribution of the expected oligomer peak. In other words, the relative atomic masses commonly used for the calculation of the molecular weight were used (C, 12.011; H, 1.0079; O, 15.999). The procedure for obtaining M_n, M_w, and Q (LOTUS 1-2-3 spreadsheet) from a representative DI mass spectrum is exemplified in Table I.

Taking this approach, FD provided the best agreement with the ^{1}H NMR reference M_n value (Table II). The lower value obtained by DEI is probably due to the pyrolysis reaction that should increasingly affect higher molecular weight oligomers. The slightly higher value furnished by K^+IDS may be due to the time lag for the production of the ionizing K^+ species.[51] During this time lag, the analyte may experience sufficient heating that some of the more volatile sample constituents (most notably phenol and the dimer) have already been evaporated. The bias in the TSP mass spectrum may also be related to the evaporation and removal of low molecular weight sample constituents from the droplets before they can reach the region of the ion source that is sampled by the quadrupole analyzer (through an orifice).

The reproducibility of the molecular weight averages calculated from DI mass spectra has also been a subject of our study. In general, the reproducibility should basically be determined by the number of scans that can be acquired and averaged from a single sample. TSP (filament-on) ionization was selected as an appropriate model, because we were able to control the number of accumulated scans. The Novolak-type resin was dissolved in the TSP solvent, and the solution was supplied to the ion source at 1 mL/min flow rate. The M_n values calculated from single scans revealed a standard deviation of ±24 (6.4% of the average). After 10 successive scans were accumulated, the standard deviation was below ±17 (4.5%). These reproducibility data are related to constant sample supply. The standard deviation was somewhat larger, when the samples were injected through a loop (flow injection). The relative standard deviation always was below 10% ($M_n = 375 \pm 34$) upon accumulating five or more mass spectra from the injection profile. Similar, or better, reproducibility was also achieved with the other DI techniques (DEI, FD, K^+IDS).

Resol-Type Resin. The composition of the base-catalyzed condensation product of phenol and formalde-

Table I
Average Molecular Weight and Polydispersity Calculation[a]
from the FD Mass Spectrum of the Novolak-Type
Phenol–Formaldehyde Resin

M_i (m/z)	N_i[b]	N_iM_i	$N_iM_i^2$	note
		(A) From Raw Data		
81	3.2	259.2	20 995.2	
94	39.3	3694.2	347 254.8	M[·+], phenol
95	8.1	769.5	73 102.5	c
96	0.9	86.4	8 294.4	c
100	24.8	2480	248 000	M[2+], dimer
100.5	6.9	693.45	69 691.7	c
101	1.2	121.2	12 241.2	c
117	1.3	152.1	17 795.7	
128	0.7	89.6	11 468.8	
133	0.8	106.4	14 151.2	
153	12.1	1851.3	283 248.9	M[2+], trimer
153.5	4.3	660.05	101 317.7	c
154	1.2	184.8	28 459.2	c
164	0.8	131.2	21 516.8	
173	2.2	380.6	65 843.8	
199	4.9	975.1	194 044.9	
200	100	20000	4 000 000	M[·+], dimer
201	16.5	3316.5	666 616.5	c
202	3.4	686.8	138 733.6	c
203	0.9	182.7	37 088.1	c
206	7.0	1442	297 052	M[2+], tetramer
206.5	3.3	681.45	140 719.4	c
207	1.1	227.7	47 133.9	c
213	1.6	340.8	72 590.4	
223	1.3	289.9	64 647.7	
238	2.2	523.6	124 616.8	
257	2.5	642.5	165 122.5	
271	0.8	216.8	58 752.8	
295	1.0	295	87 025	
305	6.3	1921.5	586 057.5	
306	86.9	26591.4	8 136 968	M[·+], trimer
307	22.3	6846.1	2 101 753	c
308	4.1	1262.8	388 942.4	c
332	2.0	664	220 448	
345	1.2	414	1 428 30	
363	1.8	653.4	237 184.2	
381	1.4	533.4	203 225.4	
399	0.9	359.1	143 280.9	
411	3.7	1520.7	625 007.7	
412	50.6	20847.2	8 589 046	M[·+], tetramer
413	16.3	6731.9	2 780 275	c
414	3.8	1573.2	651 304.8	c
435	1.5	652.5	283 837.5	
472	0.7	330.4	155 948.8	
503	1.0	503	253 009	
517	1.4	723.8	374 204.6	
518	12.4	6423.2	3 327 218	M[·+], pentamer
519	5.1	2646.9	1 373 741	c
520	1.8	936	486 720	c
623	0.8	498.4	310 503.2	
624	6.2	3868.8	2 414 131	M[·+], hexamer
625	2.9	1812.5	1 132 813	c
626	0.9	563.4	352 688.4	c
730	2.1	1533	1 119 090	M[·+], heptamer
731	1.3	950.3	694 669.3	c
	493.7	132841.8	44 502 422	$(\Sigma N_i, \Sigma N_iM_i, \Sigma N_iM_i^2)$

$$M_n = 269.0 \ (132841.8/493.7)$$
$$M_w = 335.0 \ (44502422/132841.8)$$
$$Q = 1.24 \ (335.0/269.0)$$

M_i (m/z)	N_i[b]	N_iM_i	$N_iM_i^2$	note
		(B) From Molecular Ions		
94.108	39.3	3698.4	348 053	(N_{94})
200.226	124.8	24988.2	5 003 288	$(N_{200} + N_{100})$
306.344	99.0	30328.1	9 290 817	$(N_{306} + N_{153})$
412.462	57.6	23757.0	8 608 320	$(N_{412} + N_{206})$
518.58	12.4	6430.4	3 334 673	(N_{518})
624.698	6.2	3873.1	2 419 535	(N_{624})
730.816	2.1	1534.7	1 121 593	(N_{730})
	341.4	94610.7	31 317 154	$(\Sigma N_i, \Sigma N_iM_i, \Sigma N_iM_i^2)$

$$M_n = 277.1 \ (94610.7/341.4)$$
$$M_w = 331.0 \ (31317154/94610.7)$$
$$Q = 1.19 \ (331.0/277.1)$$

[a] Lotus 1-2-3 spreadsheet. [b] Relative abundance (percentage of base peak intensity). [c] Isotope ions (^{13}C and ^{18}O).

hyde[26] is substantially more complex than that of the Novolak-type resin.[25] There is no single formula that could generally describe the structure of oligocondensates. In

Table II
Calculated Molecular Weight Averages and Polydispersity
from DI Mass Spectra of Novolak-Type
Phenol–Formaldehyde Resin[a]

	method A[b]			method B[c]		
	M_n	M_w	Q	M_n	M_w	Q
DEI	207	275	1.33	236	300	1.27
TSP[d]	388	462	1.19	375	462	1.07
K$^+$IDS	318	367	1.15	316	366	1.15
FD	269	335	1.25	277	331	1.19

[a] $M_n = 279$ is obtained from the ^{1}H NMR spectrum. [b] From raw data. [c] Corrected value, calculated as described in the text. [d] Filament-on mode.

Scheme I, we illustrated how the reaction proceeds. Thus, the phenol and the polynuclear phenols identical to those found in the Novolak may be considered the skeleton of the molecules, and they usually incorporate one or more methylol substituents. There is a significant consequence of this molecular architecture. The molecules are no longer thermally stable, and the resol-type resin is a thermosetting material.

Only FD has been applicable directly to the intractable base-catalyzed condensation product. The other methods revealed serious thermal decomposition during sample introduction (DEI, DCI, K$^+$IDS) or do not yield sample-related ions (FAB). However, the spectrum given in Figure 7 is rather complex. Odd-electron molecular ions (M[·+]), which are products of a vaporization–gas-phase ionization (by the high electric field, i.e. FI) sequence, as in the case of the Novolak resin, appear to be more favored for low molecular weight condensates. Fragmentation giving rise to the appearance of [M – OH]$^+$ ions can be confined to the presence of methylol substituents attached to the phenolic nuclei. This can be attributed to field dissociation—a process that has been reported to occur at high electric field for poly(ethylene glycol).[52] Although the cleavage site is per se different, similar mechanistic interpretation may be given. After the removal of the electron from the aromatic moiety (the molecule approaches the field-enhancing microneedle from the gas phase and becomes ionized by an FI process), the molecular ion may remain partially adsorbed to the surface of the emitter, and its orientation in the high electric field tends to weaken the benzylic C–O bond. Ultimately, it leads to the cleavage observed.

The high-field processes are gradually replaced by a lower-field mechanism of ionization upon proceeding toward higher molecular weight condensates. For this mechanism called desolvation,[53] only moderately high (>10^7 V m^{-1}) field strength may be necessary to extract preformed [M + Na]$^+$ and [M + Na + H$_2$O]$^+$ species from the viscous sample layers deposited onto the emitter. Sodium is a constituent of the catalyst, while water could not be completely removed from the resin.

Table III lists the oligomers identified in the resol-type phenol–formaldehyde resin, and also the corresponding ions in the FD mass spectrum. The complexity of the spectrum makes any attempt to quantitatively characterize the molecular weight distribution complicated and unreliable. Besides, higher-mass condensation products seem to be overrepresented in the spectrum, as suggested by the ^{1}H NMR average molecular weight data.

Peracetylation, which is also used for the quantitative characterization of the resol-type phenol–formaldehyde resin by ^{1}H NMR spectrometry, has been a suitable derivatization technique that affords the registration of FD spectra, shown in Figure 8. This can better be applied to obtain the molecular weight averages and polydispersity. The molecular weight is incremented by 42 upon substi-

Scheme I
Progress of the Condensation of Phenol and Formaldehyde under Base-Catalyzed Conditions[a]

Mononuclear   Binuclear
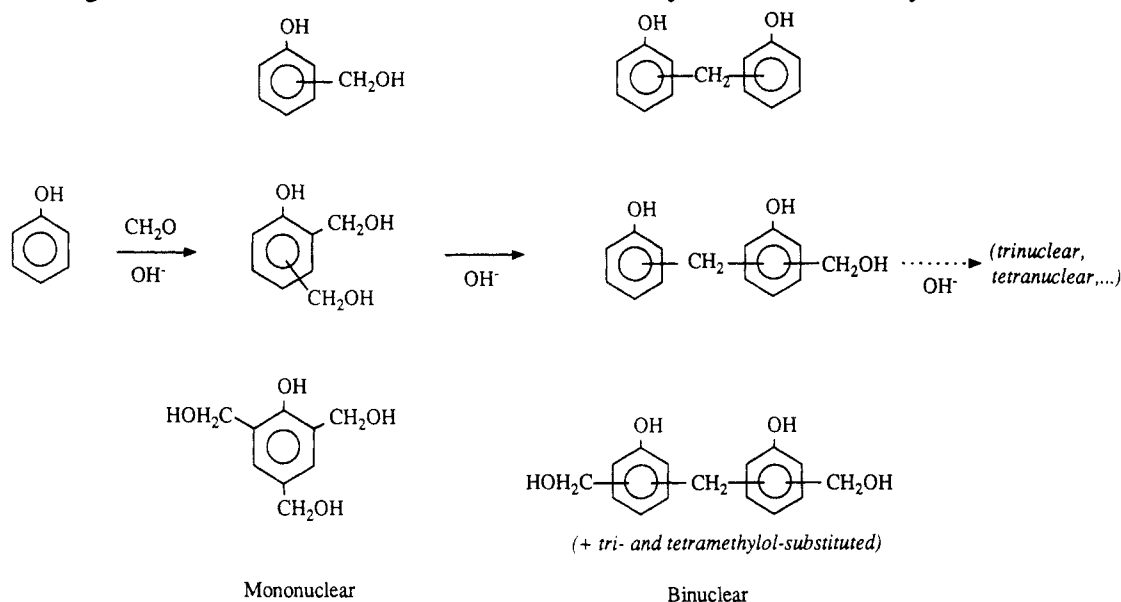
[a] The reaction is initiated with methylolation of phenol ([P]) leading to mononuclear compounds (denoted $[P][M]_m$, where [M] represents the methylol substituent and $m = 1, ..., 3$ is the number of $-CH_2OH$ groups per molecule). Binuclear ($[P]_2[M]_m$, $m = 0, ..., 4$), trinuclear, etc. compounds are formed by subsequent condensation/substitution reactions.
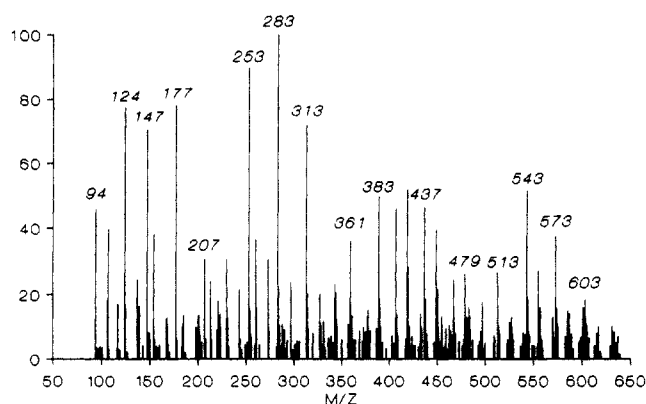

Figure 7. FD mass spectrum of the resol-type phenol-formaldehyde resin.

tuting the hydrogen of an OH group with an acetyl (CH_3CO). Thus the total increase in the molecular weight is determined by the sum of phenolic nuclei and methylol substituents present in the molecule. The ionization under FD conditions is now dominated by high-field processes. The evaporated sample molecules are ionized in the gas phase by FI, as it has been described for the Novolak oligomers. Field dissociation is also effected, but this leads predominantly to the acetyl ion at m/z 43, although loss of $CH_3CO^{\bullet}$ radical from the molecular ions is also observed to a lesser extent. Considering only the molecular ions of the acetyl derivatives, the calculated $M_n = 207$ is a satisfactory agreement with $M_n = 236 \pm 19$ obtained from the ^1H NMR spectrum. $M_w = 230$ and $Q = 1.11$ are obtained as other quantitative measures of the molecular weight distribution.

The resol-type resin remains still unamenable, even after the acetylation of the sample, to DEI, DCI, TSP (due to extensive fragmentation), and FAB (because the molecules are relatively nonpolar). However, K^+IDS may be considered useful when detection of molecular species with a higher degree of polymerization is intended in the condensation product, as shown in Figure 9. FD suffers from considerable background interference in this region due to the presence of incompletely derivatized oligomers, fragment ions, and competitive ionization processes (desorption of cationized molecules). Unlike FD, K^+IDS may

Table III
Identified Oligomers and Characteristic Ions in the FD Mass Spectrum of the Base-Catalyzed Condensation Product of Phenol and Formaldehyde

oligomer[a]	m/z[b]			
	M•+	[M − OH]+	[M + Na]+	[M + Na + H₂O]+
[P]	*94*	(−)	117	(−)
[P][M]	*124*	107	147	(−)
[P][M]₂	154	137	*177*	(−)
[P][M]₃	184	167	*207*	(−)
[P]₂	200	(−)	*223*	(−)
[P]₂[M]	230	213	*253*	(−)
[P]₂[M]₂	260	243	*283*	301
[P]₂[M]₃	290	273	*313*	331
[P]₂[M]₄	320	303	*343*	361
[P]₃	306	(−)	*329*	(−)
[P]₃[M]	336	319	*359*	377
[P]₃[M]₂	366	(−)	*389*	407
[P]₃[M]₃	396	(−)	*419*	437
[P]₃[M]₄	(−)	(−)	*449*	467
[P]₃[M]₅	(−)	(−)	*479*	497
[P]₄[M]₄	(−)	(−)	495	*513*
[P]₄[M]₃	(−)	(−)	525	*543*
[P]₄[M]₄	(−)	(−)	555	*573*
[P]₄[M]₅	(−)	(−)	585	*603*
[P]₅[M]₂	(−)	(−)	*601*	619
[P]₅[M]₃	(−)	(−)	*631*	649

[a] $[P]_n[M]_m$ represent an oligomer molecule with n phenolic nuclei (connected with methylene linkages) and m methylol substituents.
[b] Most intense ion for a particular $[P]_n[M]_m$ oligomer is set in *italics*.

be much less sensitive to the partially acetylated oligomers and gives no fragment ions, and ionization by the thermionic potassium is the single effective process of ionization.

Conclusion

Direct mass spectrometric analysis can be successfully applied to the quantitative and qualitative characterization of the phenol–formaldehyde oligocondensates. The selection of the appropriate DI methods and the proper sample treatment procedures affect the quality and depth of the information obtained. All the techniques included in this paper were performed on commercial sector or quadrupole instruments. The understanding of the prevailing mechanisms of ionization serves as a guideline for the evaluation of the relative merits and pitfalls of the
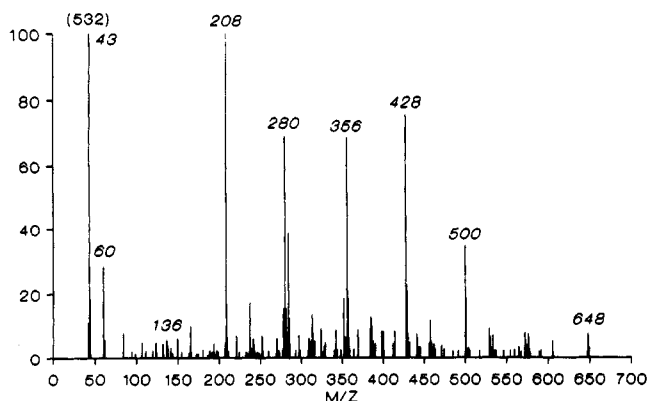
Figure 8. FD mass spectrum of the acetylated resol resin. (The peak intensities are normalized to m/z 208; m/z 43 is off-scale; the abundance is given in parentheses.)
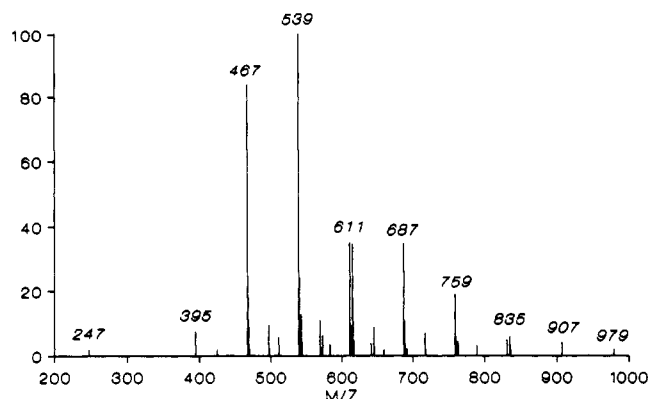

Figure 9. K⁺IDS mass spectrum of the acetylated resol-type resin.

methods involved in this study and also regarding the future efforts.

FD appears to be superior to other DI techniques for both the acid-catalyzed and base-catalyzed oligocondensates. This method offers flexibility of controlling the ionization processes through certain instrumental parameters (ion emitter, field strength), matrix interactions, or derivatization.

K⁺IDS features almost background-free mass spectra when obtainable. In quantitative terms, bias toward higher mass may be rationalized by the fact that (part of) lower molecular weight components with higher vapor pressure distill off the sample holder before the thermionic emission of ionizing potassium ions.

Although DEI, DCI, and filament-on TSP, like K⁺IDS, also apply the principle of fast evaporation of neutral molecules followed by ionization in the gas phase, these techniques may be too "energetic" to the thermally labile phenol–formaldehyde oligocondensates. The pitfalls of the conventional FAB technique may be sought in the excessive matrix interference, as well as in unfavorable sample–matrix interactions that preclude desorption of these types of molecules.

References and Notes

(1) Cooper, A. R., Ed. *Determination of Molecular Weight*; John Wiley & Sons: New York, 1989.
(2) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.
(3) Lattimer, R. P.; Harris, R. E.; Schulten, H.-R. *Rubber Chem. Technol.* **1985**, *58*, 577.
(4) Simonsick, W. J., Jr. In *Analysis of Paints and Related Materials: Current Techniques for Solving Coating Problems*; Golton, W. C., Ed.; ASTM STP 1119; ASTM: Philadelphia, 1992 (in press).
(5) Mori, S. *Anal. Chem.* **1988**, *60*, 1125.
(6) Cotter, R. J. *Anal. Chem.* **1980**, *52*,1589A.
(7) Beckey, H. D. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 500.
(8) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F. *Mass Spectrom. Rev.* **1990**, *9*, 37.
(9) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. *J. Chem. Soc., Chem. Commun.* **1981**, 325.
(10) Aberth, W.; Straub, K. M.; Burlingame, A. L. *Anal. Chem.* **1982**, *54*, 2029.
(11) Hercules, D. M.; Day, R. J.; Balasanmugam, K.; Dang, T. A.; Li, C. P. *Anal. Chem.* **1982**, *54*, 280A.
(12) Hillenkamp, F. *Adv. Mass Spectrom.* **1989**, *11A*, 354.
(13) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776.
(14) Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 1255.
(15) Lattimer, R. P.; Schulten, H.-R. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 105.
(16) Lattimer, R. P.; Schulten, H.-R. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 277.
(17) Saito, J.; Toda, S.; Tanaka, S. *Bunseki Kagaku* **1980**, *29*, 462.
(18) Saito, J.; Hara, J.; Toda, S.; Tanaka, S. *J. Appl. Polym. Sci.* **1983**, *28*, 2303.
(19) Saito, J.; Waki, H.; Teramae, N.; Tanaka, S. *Prog. Org. Coat.* **1988**, *15*, 311.
(20) Ballisteri, A.; Garozzo, D.; Giuffrida, M.; Montaudo, G. *Anal. Chem.* **1987**, *59*, 2024.
(21) Montaudo, G. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 95.
(22) Lattimer, R. P.; Harris, R. E.; Schulten, H.-R. In *Determination of Molecular Weight*; Cooper, A. R., Ed.; John Wiley & Sons: New York, 1989; Chapter 14, p 391.
(23) Woodbrey, J. C.; Higginbottom, H. P.; Culbertson, H. M. *J. Polym. Sci.* **1965**, *A3*, 1079.
(24) Rudin, A.; Fyfe, C. A.; Vines, S. M. *J. Appl. Polym. Sci.* **1983**, *28*, 2611.
(25) Prokai, L. *J. Chromatogr.* **1985**, *329*, 290.
(26) Prokai, L. *J. Chromatogr.* **1985**, *331*, 91.
(27) Prokai, L. *J. Chromatogr.* **1985**, *333*, 161.
(28) Prokai, L. *J. Chromatogr.* **1986**, *356*, 331.
(29) Mori, S.; Saito, T.; Takeuchi, M. *J. Chromatogr.* **1989**, *487*, 181.
(30) Werner, W.; Barber, O. *Chromatographia* **1982**, *15*, 101.
(31) Mechin, B; Hanton, D.; Le Goff, J.; Tanneur, J. P. *Eur. Polym. J.* **1984**, *20*, 333.
(32) Mechin, B.; Hanton, D.; Le Goff, J.; Tanneur, J. P. *Eur. Polym. J.* **1986**, *22*, 115.
(33) Herman, G.; Skotnicki, P.; Weston, A. F. *Proceedings of the 30th Annual (ASMS) Conference on Mass Spectrometry and Allied Topics*, Honolulu, HI, 1982; p 636.
(34) Saito, J.; Toda, S.; Tanaka, S. *Netsu Kokasei Jushi* **1981**, *2*, 72.
(35) Prokai, L. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 223.
(36) Schulten, H.-R.; Beckey, H. D. *Org. Mass Spectrom.* **1972**, *6*, 885.
(37) Beckey, H. D.; Heindrichs, A.; Winkler, H. U. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *3*, 9.
(38) Simonsick, W. J., Jr. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1989**, *43*, 257.
(39) Simonsick, W. J., Jr. *Prog. Org. Coat.* **1992**, *20*, 411.
(40) Lotus 1-2-3, Release 2.2, Lotus Development Corp., Cambridge, MA.
(41) Martinez, J.; Guichon, G. *J. Gas Chromatogr.* **1967**, *5*, 146.
(42) Prokai, L. Unpublished results.
(43) Vestal, M. L. *Mass Spectrom. Rev.* **1983**, *3*, 521.
(44) Light, K. J.; Kassel, D. B.; Allison, J. In *Proceedings of the 35th ASMS Conference on Mass Spectrometry and Allied Topics*, Denver, CO, 1987; p 733.
(45) Prokai, L. *Field Desorption Mass Spectrometry*; Marcel Dekker: New York, 1990; Chapter 1.
(46) Giessmann, U.; Stoll, R.; Röllgen, F. W. *Adv. Mass Spectrom.* **1980**, *8*, 1047.
(47) Röllgen, F. W.; Heinen, H. J. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 92.
(48) De Pauw, E. *Mass Spectrom. Rev.* **1986**, *5*, 191.
(49) Bojesen, G.; Moller, J. *Int. J. Mass Spectrom. Ion Processes* **1986**, *68*, 239.
(50) Cooks, R. G.; Busch, K. L. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 111.
(51) Light, K. L.; Kassel, D. B.; Allison, J. *Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics*, San Francisco, CA, 1988; p 1213.
(52) McCrae, C. E.; Derrick, P. J. *Org. Mass Spectrom.* **1983**, *18*, 321.
(53) Wong, S. S.; Giessmann, U.; Karas, M.; Röllgen, F. W. *Int. J. Mass Spectrom. Ion Processes* **1984**, *56*, 139.