# Structural Characterization of Polyester Resins by Electrospray Mass Spectrometry

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## SYNOPSIS

Sixteen different polyester paint resins have been examined by electrospray ionization mass spectrometry (ESI-MS) in a novel application of the technique for structural analysis of polyesters. Synthetic resins typically contain a range of polymeric structures comprised of various ratios of the monomeric components. When polyesters are analyzed by ESI-MS, singly and doubly charged ions are produced and oligomeric species of the polyesters can be clearly identified. The addition of alkali metal salts to the polyester samples and modification of the solvent system was also found to dramatically enhance the ESI-MS efficiency of polyesters. The ESI mass spectra enabled identification of the range and relative abundance of chemical structures present in each sample. Using this information, average molecular weights, polydispersity, the distribution of acid versus alcohol end groups, overall monomer proportions, average functionality per molecule, and average frequency of branching per molecule have been calculated. The identities of peaks in the ESI-MS spectra have been confirmed by tandem mass spectrometry. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polyester resins comprised of diacid, diol, and polyol monomers are used in many paint formulations which serve as protective and decorative surface coatings for metal products including building materials and metal appliances. Structural characterization of the components of these resins is important for the development of coatings with improved durability and performance. Mass spectrometry has been shown to be useful in determining chemical properties of the paint resins, and it can also assist in the identification of paint type and source. Polyester resins have been previously examined by a range of mass spectrometric techniques including direct pyrolysis (DP),[1-4] field desorption (FD),[5,6] and fast atom bombardment (FAB).[7-11] However, these techniques have fundamental limitations. For example, direct pyrolysis results in extensive fragmentation of the sample molecules and with FD and FAB, only relatively low-molecular-weight species have been detected.[7-10] Other soft ionization techniques such as laser desorption (LD) and matrix-assisted laser desorption ionization (MALDI) have also been used to determine molecular weight and structural information for a variety of synthetic polymers[12,13] up to 10,000 Da.[14] Electrospray ionization mass spectrometry (ESI-MS) was developed for mass spectral analysis of organic molecules by Fenn et al.[15,16] following the pioneering work of Dole[17] and has recently found extensive application in the structural analysis of large biopolymers, especially proteins.[18,19] In marked contrast, only a few studies have appeared describing the ESI mass spectrometry of synthetic polymers.[20-23]

We report here the results of the analysis of 16 different polyesters by ESI-MS focusing on the structural information that can be derived from this technique. In separate work we examine in detail the influence of ESI-MS conditions on the molecular weight distributions derived from this method.[24]

## EXPERIMENTAL

Electrospray mass spectra were recorded using a VG Quattro mass spectrometer. This is a tandem mass

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**Table I Names, Abbreviations, and Molecular Weights of the Various Constituent Monomers of the Polyester Resins**

| Monomer | Abbreviation | Molecular Weight |
|---|---|---|
| Adipic acid | ADA | 146.06 |
| 1,3-Cyclohexane dicarboxylic acid | 1,3-CHDA | 172.07 |
| 1,4-Cyclohexane dicarboxylic acid | 1,4-CHDA | 172.07 |
| 3,3-Dimethylglutaric acid | DMG | 160.17 |
| 2,2,4-Trimethyl-1,3-pentane diol | TMPD | 146.13 |
| Trimethylolpropane | TMP | 134.09 |
| Neopentylglycol | NPG | 104.08 |
| 2-Butyl-2-ethyl-1,3-propanediol | BEPD | 160.15 |
| 1,4-Cyclophexanedimethanol | CHDM | 144.12 |
| Hydroxypivalylhydroxypivalate | HPHP | 204.14 |

spectrometer with 4000 mass range quadrupole mass analyzers for MS1 and MS2 and a hexapole collision cell (VG Biotech, Altrincham, UK). Initially, the polyester reins were dissolved in acetone (25 mg/mL) and diluted to 2.5 mg/mL in 50% methanol/water. Likewise the solvent stream used for delivery of the samples to the instrument was 50% methanol/water. Subsequent work employed dilutions of the polyester stock solutions to 2.5 mg/mL in a solution of 0.012*M* sodium acetate in 90% acetone/water, acetone was used as the solvent stream. The solvent was delivered to the ESI-MS source by an ISCO (Lincoln, NE, USA) SFC-500 syringe pump at a flow rate of 5 $\mu$L/min and 10 $\mu$L of polyester solution were injected for each analysis. A dry nitrogen bath gas at atmospheric pressure was employed to assist evaporation of the electrospray droplets. The electrospray probe tip potential was 3.5 kV with 0.5 kV on the chicane counter electrode. A skimmer potential of 30 V, used for initial analyses was increased to 125 V for analysis of sodiated samples. The skimmer potential acts to focus the ions through a skimmer in the ESI ionisation source, and it determines the degree of acceleration and hence collisional activation in the intermediate pressure region in the source. With higher skimmer potentials more fragmentation is usually observed.[25]

Both MS1 and MS2 spectra were obtained with a resolution of ~ 1 Da and a photomultiplier voltage of 650 V. Tandem mass spectrometry (MS/MS) experiments involve mass selection of an incident ions by MS1. These are then passed through a collision cell where they undergo collisions with an inert gas and subsequently fragment. These fragments are detected in MS2, thus yielding structural information concerning the mass-selected incident ions. For MS/MS experiments, argon collision gas was used at a pressure corresponding to 30% transmission of the incident ion beam and a collision energy of 75 eV. MS1 and MS2 were typically scanned at a rate of 1 s per 100 Da. Data from 10 scans were summed to obtain representative spectra.

## RESULTS AND DISCUSSION

### Nomenclature

All of the polyester resins used in this study were synthesized by condensation of a diacid (A), a diol (B), and a small proportion of triol (T) with the exception of resin number 37 which combined a diacid and diol only. The various monomers, their full chemical names and their abbreviated names, are given in Table I. The monomer combinations in individual oligomers are denoted by combinations of these, e.g. $(2A + 2B + T)H^+$, and the oligomeric series to which this belongs is indicated by the expression $[(x)A + (x + 1)B]Na^+$.

### Initial Results

In our preliminary study,[20] ESI-MS spectra were obtained from polyester solutions prepared in 50% aqueous methanol, injected into a 50% aqueous methanol solvent stream, since this was the solvent system most commonly used in our laboratory. These spectra showed a range of singly charged polymeric structures, corresponding to several different polyester oligomer series.[20] For example, Figure 1(a) shows the electrospray mass spectrum of polyester number 20 which is a combination of TMPD, 1,4-CHDA and a small proportion of TMP. The base peak at *m/z* 429 in Figure 1(a) corresponds

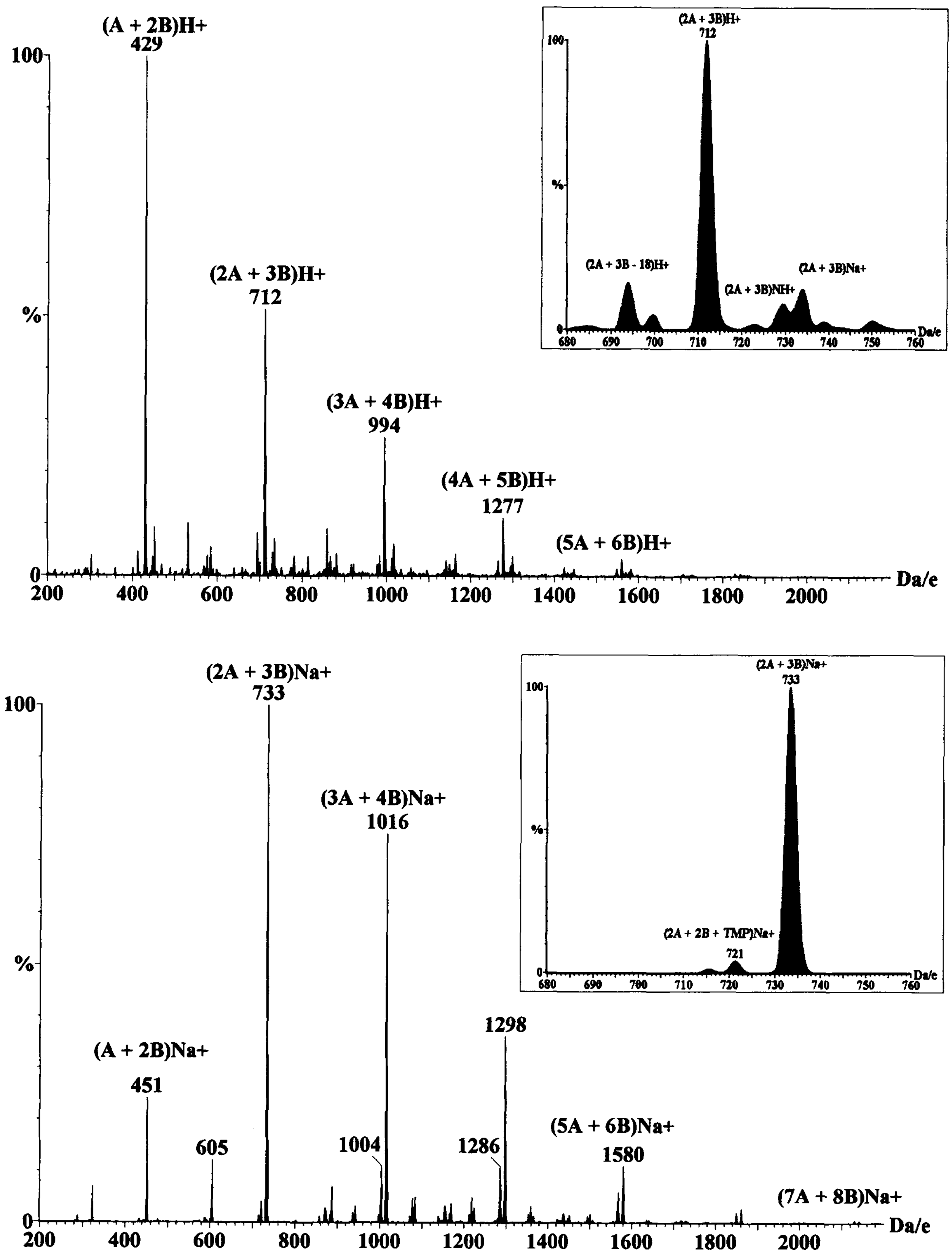

**Figure 1** Electrospray mass spectrum for polyester resin number 20 (formulated from 1,4-cyclohexanedicarboxylic acid, 2,2,4-trimethyl-1,3-pentane diol and a small amount of trimethylolpropane): (a) in 50% aqueous methanol, skimmer potential 30 V and (b) in 90% aqueous acetone doped with sodium acetate, skimmer potential 125 V.

to the $(A + 2B)H^+$ oligomer, a combination of one 1,4-CHDA diacid and two TMPD diol monomers with a charge state of $^+1$ acquired by proton attachment. This is the first oligomer in the dominant $[(x)A + (x + 1)B]H^+$ series which also includes peaks at *m/z* 712, 994, and 1275, and the highest peak at *m/z* 1557 corresponding to the $(5A + 6B)H^+$ combination. A weaker series of the form $[(x)A + (x)B]H^+$ is also observed with *m/z* 865 the largest peak in the series.

A significant feature of the polyester resin ESI-MS obtained in aqueous methanol was the multiplicity of peaks, as each polyester species forms a number of different adducts due to attachment of $H^+$, $Na^+$, and $NH_4^+$ cations. The detection of adducts of alkali metals is commonly observed with all soft ionization mass spectrometry methods and requires only trace amounts of the cations, which are present in samples, solvents, etc. This is illustrated in the expanded view of the *m/z* 712 peak in Figure 1(a). The peak assigned to the $(2A + 3B)H^+$ oligomer is accompanied by sodium and ammonium adducts as well as the dehydrated form of the polyester. The presence of these multiple adducts both complicates the polyester ESI-MS spectra and masks the presence of some less abundant species, as the ion current for these are distributed over a number of peaks and therefore is weak and/or below the detection limit.

## Optimum Conditions

Following a thorough investigation of the effects of various solvents (e.g., acetone, isopropanol, tetrahydrofuran, methylethylkoetone), and the addition of alkali metal cations, an optimum set of analysis conditions was developed. Acetone replaced methanol/water as a sample solvent due to concern about the solubility of the resins in an aqueous medium, and we also found it was important for acetone to be used for the solvent delivery, to prevent diffusion and deposition of the sample in the injection system due to differences in the sample solvent and the solvent stream (for other types of systems this is not always critical). Sodium acetate was added to the sample matrix to concentrate the ion current for each oligomer as one adduct. Finally, the optimum skimmer potential used for the analysis of the sodiated solutions was found to be much higher than that used initially.

One example of these subsequent spectra which were obtained from polyester solutions prepared in acetone, doped with sodium acetate, and recorded with a high skimmer potential is the ESI-MS spectrum for resin number 20, given in Figure 1(b). The signal-to-noise ratio and ion intensity is superior to the previous spectrum for the same polyester [e.g., Figure 1(a)]. Further, all the polyester species are only observed as sodium adducts, as illustrated by the expanded view of the *m/z* 733 peak, assigned to $(2A + 3B)Na^+$. This peak has no other associated adducts and the less intense $(2A + 2B + T)Na^+$ species is now clearly visible, whereas this oligomer was not detected in Figure 1(a). A much higher mass range is observed under these optimum conditions; the highest singly charged species in Figure 1(b) is $(7A + 8B)Na^+$ at *m/z* 2143 compared to a maximum of *m/z* 1557 for $(5A + 6B)H^+$ in Figure 1(a). However, this range is considerably extended by the formation of doubly charged species, the $[(x)A + (x + 1)B]2Na^+$ and $[(x)A + (x)B + T]2Na^+$ series beginning at *m/z* 802 for $(5A + 6B)2Na^+$ which corresponds to an oligomer mass of 1559 Da and reaching a maximum of *m/z* 1783 for $(12A + 12B + T)2Na^+$ which corresponds to an oligomer mass of 3519 Da. Multiply charged species are a common feature of the ESI-MS spectra of other compound classes.[16]

## Tandem Mass Spectrometry

Tandem mass spectrometry (MS/MS) was performed on a number of the major ions in the ESI-MS spectra of the polyester resins to verify the structures assigned to each peak. For example, Figure 2 shows the MS/MS spectrum of the *m/z* 733 ion in the sodiated acetone solution of polyester resin number 20. This ion was assigned to $(2A + 3B)Na^+$ (A = 1,4-CHDA and B = TMPD) and the MS/MS spectrum displays peaks characteristic of this monomer combination. A strong peak was seen at *m/z* 605 for the $(2A + 2B)Na^+$ fragment, weaker peaks were observed at *m/z* 477 for $(2A + B)Na^+$, *m/z* 433 for $(A + 2B)Na^+$, *m/z* 323 for $(A + B)Na^+$, and *m/z* 195 for $(A)Na^+$ fragments. These results demonstrate the utility of MS/MS to confirm the peak assignments for the polyester resins. The ion intensity and signal-to-noise ratios in the MS/MS spectra obtained for sodiated acetone samples were also superior to the corresponding spectra obtained from aqueous methanol samples, demonstrating a marked improvement in MS/MS results by using the optimized conditions.

## Structural Characterization and Molecular Weight Calculations

A range of different polyester resins were analyzed using the optimized method of analysis; these results

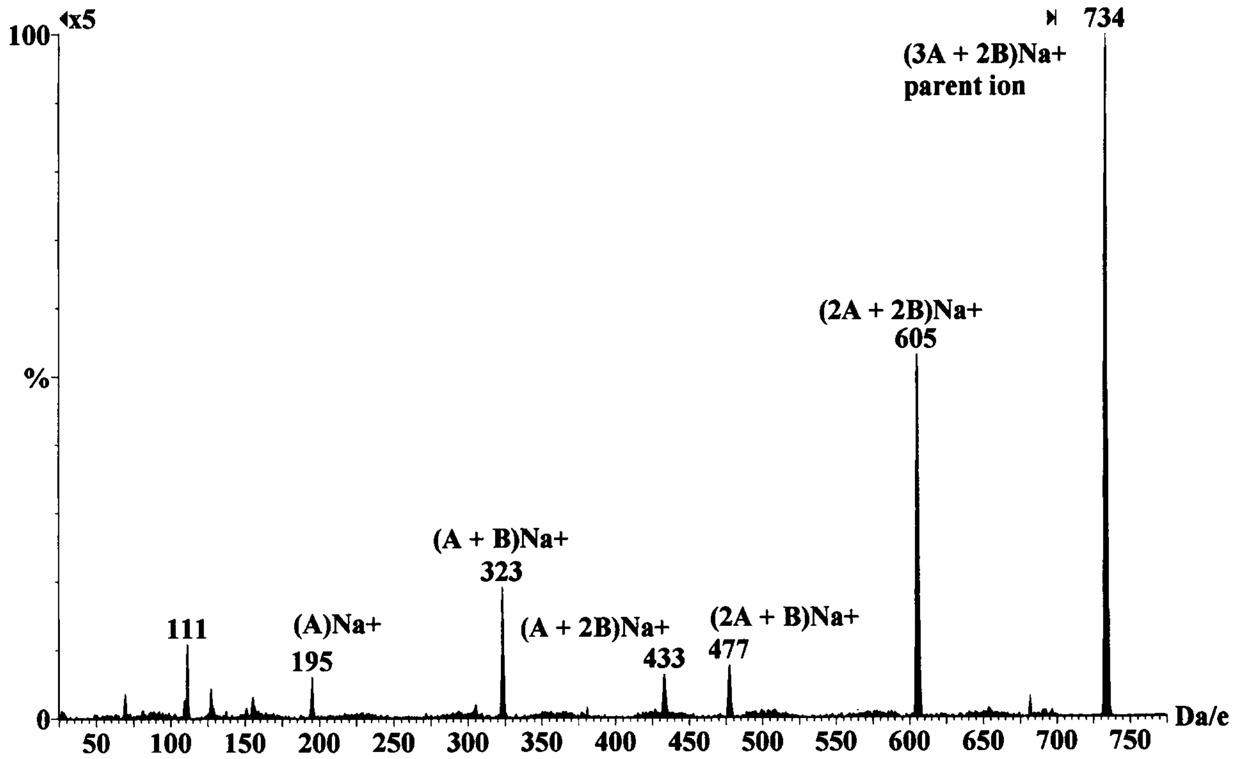

**Figure 2** MS/MS spectrum of $m/z$ 733 assigned $(2A + 3B)Na^+$ for polyester resin number 20 (formulated from 1,4-cyclohexanedicarboxylic acid, 2,2,4-trimethyl-1,3-pentane diol and a small amount of trimethylolpropane). Laboratory collision energy 30% transmission argon.

are summarized in Table II. For each resin the major and minor ion series were assigned to 13 different oligomer types, indicated in the ion series key. In each case, $[(x)A + (x + 1)B]Na^+$ was the most intense series and the $[(x)A + (x)B - 18]Na^+$ consistent with loss of water was observed as a major ion series in 11 of the resins. To confirm that these dehydrated oligomers are present in the sample and not formed during the ionization process, the ion current for both the $[(x)A + (x)B]Na^+$ and the $[(x)A + (x)B - 18]Na^+$ oligomers were monitored over a range of skimmer potentials. Raising the skimmer potential would increase any fragmentation such as dehydration, occurring in the ionisation region.[25] Thus, if the dehydrated oligomers were being formed in the ion source as the skimmer potential was raised, the ion current for the parent oligomer would decrease, while the ion current for the dehydrated species would increase. However, the ion current for both species optimized at the same skimmer potential, indicating that the dehydrated oligomers were present in the sample, probably as cyclic oligomers formed during synthesis as observed previous studies of polyester resins.[7,9,10]

$[(x)A + (x + 1)B]2Na^+$ and $[(x)A + (x)B + T]Na^+$ were also present as major ion series in several of the resins. For most of the resins, $(2A + 3B)Na^+$ was the base peak, with $(3A + 4B)Na^+$ and $(4A + 5B)Na^+$ also identified as base peaks for a small number of resins. Varying degrees of branching were evident by the detection of triol-containing oligomers in all of the polyesters except resin number 37 (a linear formulation). The highly branched polyester number 6 and 7 were characterized by oligomer series containing more than one triol per molecule; these resins were known to have elevated levels of triol in their formulations.

Number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) for each of the polyester samples are listed in Table II. These values were calculated using Eqs. (1) and (2),[4] the relative peak intensities ($N_i$), and molecular weight minus the mass of the cation ($M_i$) of each oligomer identified. The number-average molecular weights ranged from 1002 for resin number 6 to 1347 for resin number 37. These average molecular weights are considerably lower than those expected from the synthesis parameters.[24] However,

**Table II Summary of Polyester Resin Analyses**[a]

| Resin | Diacid (A) | Diol (B) | $M_n$ | $M_w$ | $M_w/M_n$ | Major Ion | Ion Series[b] Major | Ion Series[b] Minor |
|---|---|---|---|---|---|---|---|---|
| 2 | 1,4-CHDA | NPG | 1136 | 1429 | 1.26 | (3A + 4B)Na+ | 1,2 | 3, 4, 8, 10 |
| 3 | 1,4-CHDA | HPHP | 1108 | 1427 | 1.29 | (2A + 3B)Na+ | 1 | 2, 3, 4, 8, 10 |
| 6 | 1,4-CHDA | BEPD | 1002 | 1146 | 1.14 | (2A + 3B)Na+ | 1, 2, 5 | 4, 6, 7, 11, 12, 13 |
| 7 | 1,4-CHDA | BEPD | 1115 | 1333 | 1.20 | (2A + 3B)Na+ | 1, 2 | 3, 5, 6, 10, 11, 12, 13 |
| 14 | ADA | NPG | 1230 | 1550 | 1.26 | (4A + 5B)Na+ | 1, 3 | 4, 2, 8, 10 |
| 15 | ADA | HPHP | 1265 | 1594 | 1.26 | (2A + 3B)$Na^+$ | 1, 3, 8 | 10, 2 |
| 16 | DMG | NPG | 1272 | 1567 | 1.23 | (3A + 4B)Na+ | 1, 3 | 2, 4, 8, 10 |
| 20 | 1,4-CHDA | TMPD | 1079 | 1316 | 1.22 | (2A + 3B)Na+ | 1 | 2, 4, 8, 10 |
| 21 | DMG | HPN | 1222 | 1540 | 1.26 | (2A + 3B)Na+ | 1, 3, 8 | 2, 4, 9, 10 |
| 22 | DMG | NPG | 1190 | 1551 | 1.30 | (3A + 4B)Na+ | 1, 3 | 2, 8, 10 |
| 23 | 1,3-CHDA | HPHP | 1278 | 1678 | 1.31 | (2A + 3B)Na+ | 1, 3, 8 | 2, 4, 10 |
| 24 | 1,4-CHDA | 1,4-CHDM | 1176 | 1662 | 1.41 | (2A + 3B)Na+ | 1, 2, 3, 8 | 4, 10 |
| 25 | 1,4-CHDA | BEPD | 1259 | 1618 | 1.29 | (2A + 3B)Na+ | 1, 3 | 2, 4, 8, 10 |
| 26 | 1,3-CHDA | BEPD | 1283 | 1638 | 1.28 | (2A + 3B)Na+ | 1, 3 | 2, 4, 8, 10 |
| 27 | ADA | BEPD | 1345 | 1708 | 1.27 | (3A + 4B)Na+ | 1, 3, 8 | 2, 4, 10 |
| 37 | ADA | NPG | 1347 | 1655 | 1.23 | (4A + 5B)Na+ | 1, 3, 4, 8, 9 | |

Key to Ion Series[c]

Singly Charged

1. [($x$)A + ($x$ + 1)B]NA+
2. [($x$)A + ($x$)B + T]Na+
3. [($x$)A + ($x$)B − 18]Na+
4. [($x$)A + ($x$)B]Na+
5. [($x$)A + ($x$ − 1)B + 2T]Na+
6. [($x$)A + ($x$ − 2)B + 3T]Na+
7. [($x$)A + ($x$ − 3)B + 4T]Na+

Doubly Charged

8. [($x$)A + ($x$ + 1)B]2Na+
9. [($x$)A + ($x$)B]2Na+
10. [($x$)A + ($x$)B + T]2Na+
11. [($x$)A + ($x$ − 1)B + 2T]2Na+
12. [($x$)A + ($x$ − 2)B + 3T]2Na+
13. [($x$)A + ($x$ − 3)B + 4T]2Na+

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[a] All resins except no. 37 also incorporate a small amount of TMP triol in their formulation.

[b] Major ion series have at least one component > 20% of base peak intensity, minor ion series are all < 20%.

[c] $x$ is an integer representing the relative proportions of monomers in an ion series.

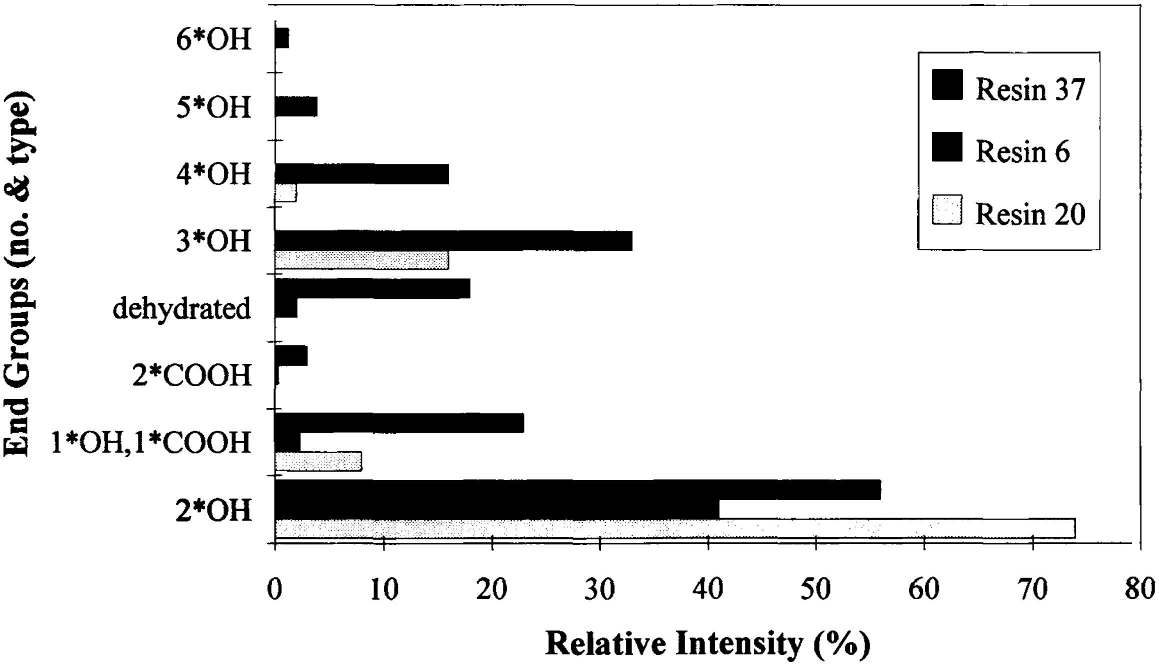

**Figure 3** Number and type of end groups vs. relative intensity in ESI mass spectra for three polyester resins (Table II).

the latter may be subject to error as they rely on acid value titrations and the assumption that the monomer proportions remain constant during synthesis, whereas monomer loss frequently occurs at the elevated synthesis temperatures.

$$M_n = \sum N_i M_i / \sum N_i \quad (1)$$

$$M_w = \sum N_i M_i^2 / \sum N_i M_i \quad (2)$$

## End-Group Analysis

One important structural feature of polyesters which are to be formulated into paint coatings is the proportion of alcohol versus acid end groups, since when the latter reacts with crosslinker, the resulting resin is more susceptible to hydrolysis. As ESI-MS indicates the monomer composition of oligomers present in the polyester resin, the ratio of diol to dicarboxylic acid monomers in these oligomers can be used to determine their end-group functionality. Linear polyester chains have two end groups which may be both hydroxy or both carboxy, or alternatively, one of each. Oligomers which incorporate a tri-functional branching agent (such as TMP) will have three end groups for which there are four possible combinations, these being three hydroxy, three carboxy, two hydroxy-one carboxy, or two carboxy-one hydroxy. ESI-MS spectra of the polyester resins were analyzed to determine the nature of oligomer end groups, and their relative proportions in the polyester resins. The results for resins 20, 6, and 37 are shown in Figure 3.

Resin 20 was formulated to have an excess of hydroxyl end groups; this feature is reflected in the end-group analysis figures as the dihydroxy end groups are the most abundant, with a small amount of hydroxy-carboxylic end groups and no dicarboxylic end groups detected. Branching is also present in this resin in the form of trihydroxy and some tetrahydroxy groups. Resin 6 was also formulated for excess hydroxyl groups combined with a high degree of branching (high TMP content). Corresponding to this, the end-group analysis for resin 6 showed very little carboxyl functionality with very small amounts of hydroxy-carboxylic, dicarboxylic, and dehydrated hydroxy-carboxylic groups and a large number of hydroxy functional groups were detected as di-, tri-, tetra-, and hexa-hydroxy species. The highly branched nature of the resin was reflected in the large number of di- to hexa-functional molecules detected. Resin 37 is a linear polyester and was formulated with equal amounts of diol and diacid monomers. This is reflected in the proportions of end groups detected for this resin; considerable numbers of carboxy functional molecules were identified in the form of dicarboxy, carboxy-hydroxy, and dehydrated carboxy-hydroxy end groups. The slight

**Table III Composition and Structural Properties of Polyester Resins**

| | Resin 20 | | Resin 6 | | Resin 37 | |
|---|---|---|---|---|---|---|
| Resin Properties | Syn.[a] | ESI[b] | Syn.[a] | ESI[b] | Syn.[a] | ESI[b] |
| % Diol | 47 | 55 | 35 | 45 | 50 | 52 |
| % Diacid | 48 | 43 | 48 | 43 | 50 | 48 |
| % Triol | 5 | 2 | 17 | 12 | 0 | 0 |
| Hydroxy/molecule | 2.72 | 2.08 | 4.78 | 2.74 | 1.00 | 1.35 |
| Carboxy/molecule | 0.27 | 0.1 | 0.27 | 0.03 | 1.00 | 0.29 |
| Functionality/molecule | 2.99 | 2.18 | 5.05 | 2.78 | 2.00 | 1.64 |
| Branches/molecule | 0.99 | 0.18 | 3.05 | 0.82 | 0.00 | 0.00 |

[a] Properties calculated from synthesis data.

[b] Properties calculated from electrospray mass spectra.

excess of hydroxy groups, noted for this resin, may be due either to monomer loss during synthesis or a consequence of the diacid being less reactive than the diol.

## Comparison of Synthesis Data to ESI-MS Calculations

From their ESI-MS spectra, the polyester resins were found to contain a range of oligomeric structures. The monomer proportions and relative peak intensities of these structures can be used to determine a number of properties for the resins which can be compared to values normally projected from synthesis data. Table III shows a number of these comparisons for three of the polyester resins. When overall monomer proportions were compared to those used in the synthesis of these resins, in each case, the percent diol detected by ESI-MS was higher, while the proportions of triol and dicarboxylic acid were lower than the percent (mol/mol) used in the synthesis of these resins. This may be an indication of differences in monomer reactivities causing preferential reaction of the diol monomers or arise from variations in monomer loss during synthesis due to greater volatility of the triol or diacid.

Other properties of the polyesters that are usually projected from synthesis and molecular weight data are averages of carboxy groups, hydroxy groups, functionality, and branching per molecule. The values, calculated from ESI-MS spectra for the three resins in Table III, all follow the same trends as the values projected from the synthesis data, although they are consistently lower. A number of factors may have caused the projected values to be higher than those calculated from the ESI-MS spectra. A significant proportion of cyclic oligomers were detected in the ESI-MS spectra and since these molecules do not have any end groups, they would make the actual hydroxyl or carboxyl groups per molecule less than the projected values. Also, as the projected data requires average molecular weights for their calculation, the uncertainty in this figure would affect these calculations.

## CONCLUSION

The advantages of electrospray mass spectrometry technique for analyses of synthetic polymers are numerous. ESI-MS is an absolute method of analysis, avoiding problems of calibration experienced with many classical techniques such as gel permeation chromatography, it allows identification of each species in the molecular weight distribution, not average values as with commonly used methods of molecular weight determination. ESI-MS is a soft ionization technique which prevents fragmentation and rearrangement as with other mass spectrometric techniques. Finally, we have shown that while electrospray is limited to the analysis of samples in solution and its application limited by solubility of the sample, the solutions used in the electrospray may be modified to suit the requirements of the sample, as was the case for these polyesters. Overall, ESI-MS appears to be an extremely powerful tool for the structural characterization of polyesters.

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