Development of MALDI-MS and nano-ESI-MS methodology for the full identification of poly(ethylene glycol) additives in artists' acrylic paints

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A B S T R A C T

An analytical mass spectrometric method was developed for the comprehensive characterization of the poly(ethylene glycol) (PEG) based additives present in water extracts of acrylic emulsions, acrylic emulsion paints and samples from paintings. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was used to determine the molar mass distribution (MMD), i.e., the weight average molar mass, number average molar mass and the polydispersity characteristics of the PEG compounds. Nano electrospray ionisation mass spectrometry (ESI-MS) was used to determine the end-group structures. It was possible to determine both end-groups of the PEG compounds using ESI-MS in combination with nozzle skimmer dissociation (NSD) and tandem MS (MSMS). The method development is part of a larger project of analysis of artists' paints and samples from paintings reported elsewhere. The new methodology is demonstrated here with two relevant examples of a often used PEG and an acrylic medium.

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1. Introduction

Acrylic paint is currently the most important type of synthetic paint developed for artists' use. [1]. Available in two forms, organic solvent solution and water emulsion. The first artists' acrylic paint developed in the late 1940s was acrylic resin dissolved in turpentine to make a clear solution. Acrylic emulsions, first introduced in 1953, were initially developed for use as exterior house paint. This paint was rather thin. In 1963 a new formulation was introduced with a much thicker consistency, which was nearer to artist's oil paint [1]. The basic formulation of acrylic emulsion paint is water in which acrylic polymers are emulsified with surfactants. The acrylic emulsion is produced by an emulsion polymerization technique [2]. Surfactants, based on poly(ethylene glycol) compounds (PEG), are used to keep the acrylic droplets dispersed in the water during the polymerization and storage. During drying the water evaporates and the acrylic droplets fuse together to form a continuous film [3]. The surfactants loose their function but remain in the paint film. This film may not be completely stable and problems arise when the PEG compounds start to migrate in the dried paint film. The formation of microscopic crystalline inclusions [4] as well as the formation of characteristic aggregates on the surface of the paint film [5,6] have been reported. These artefacts may influence turbidity, surface gloss, extent and nature of dirt pick-up and the sensitiv-

ity of the film to surface cleaning [4–6]. The migration behaviour and formation of inclusions and aggregates depend on the chemical and physical properties of the PEG compound. Structural characterization of the PEG compounds is imperative for the determination of the properties of the paint film. Historically, the PEG composition has changed as paints were being developed and further improved. New high sensitivity methods with a high discriminating power are therefore necessary to get more detailed information into the composition of the PEG compounds present in modern acrylic paintings.

In several studies a partial structural characterization of PEG compounds in acrylic paint has already been achieved [5–10]. The analytical techniques used include Fourier transform infra-red (FTIR) [4,5], electrospray ionisation mass spectrometry (ESI-MS) [6], size exclusion chromatography Fourier transform infra-red spectroscopy (SEC-FTIR) [7,8], pyrolysis gas chromatography mass spectrometry (PyGCMS) [8], laser desorption/ionisation mass spectrometry (LDI-MS) [9], direct temperature resolved mass spectrometry (DTMS) [9], matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) [5] and liquid chromatography electrospray ionisation mass spectrometry (LC-ESI-MS) [10]. SEC, LDI-MS, DTMS, MALDI-MS and ESI-MS provide information on the molar mass distribution (MMD). The latter four also yield some end-group information since the residual end-group mass can be calculated. FTIR can give information on the functional groups present as the end-groups. PyGCMS has been used to determine the end-group structure. None of these studies, however, gives a comprehensive analy-

sis that includes the determination of the MMD as well as the identification of the end-groups present of the PEG polymer molecule.

A potentially strong analytical polymer science tool is mass spectrometry with the soft ionization techniques of MALDI [11] and ESI [12]. The mass over charge ratio (m/z) of pseudo molecular ions can be used to determine the MMD and calculate the residual end-group mass. MALDI-MS is the preferred way to obtain a MMD since ESI promotes multiple charging which results in more complicated spectra due to overlapping peaks. Of the different ways to determine the end-groups of a polymer molecule the accurate mass determination of a cationized molecule was proven to be a powerful one [13–15]. A drawback, however, is that the information obtained relates to both end-groups combined and therefore the elemental composition and structure of the each end-group cannot be determined. One way in which both end-groups can be analyzed separately is by tandem MS (MSMS) analysis [16–19]. The polymeric backbone is fragmented and the residual masses of both end-groups can be determined separately. Structural information of the end-groups, however, cannot be obtained this way. Structural features can be determined if the fragment that contains the end-group undergoes further dissociation. For example, ESI with nozzle skimmer dissociation (NSD) combined with collision induced dissociation (CID) [20] will give relevant end-group information.

The size of samples from paintings is typically very small (less than 50 μg of solids) and as a consequence only a very small amount of PEG compound is present for analysis. Our analytical strategy consists of the application of two MS techniques to characterise water extracts of acrylic paint microsamples. MALDI analysis typically requires only few μL of dilute solution while for ESI analysis nanospray needles can be used with a typical flow of 10–80 nL/min. The methodology is illustrated with a PEG compound often used in acrylic paints (Triton-405) and on an acrylic paint medium containing PEGs with sulphated endgroups (Texicryl 13-031). The application of the methodology to a large number of acrylic media and paints from paintings is reported elsewhere [21].

2. Experimental

2.1. Materials

Polyethylene glycol 600 sulfate (CAS No. 37340-69-5) was purchased from Fluka (Buchs, Switzerland). Triton X-405 (CAS No. 9002-93-1), 2,5-dihydroxybenzoic acid (CAS No. 490-79-9), sodium iodide (CAS No. 7681-82-5) and tetrabutylammonium hydroxide (CAS No. 2052-49-5) were purchased from Aldrich (Gillingham-Dorset, United Kingdom). Triton N-57 (CAS No. 9016-45-9), Tergitol NP-9 (CAS No. 127087-87-0) and Tergitol NP-40 (CAS No. 127087-87-0) were purchased from Sigma (St. Louis, USA). Ethanol (CAS No. 64-17-5) and methanol (CAS No. 57-56-1) were purchased from Biosolve (Valkenswaard, The Netherlands). Ion exchange resin (AG® 501-X8, 20–50 mesh) (CAS No. 60177-39-1/CAS No. 69011-20-7) was purchased from Biorad (Hercules, USA). Ammonium acetate (CAS No. 631-61-8) was purchased from Janssen Chimica (Beerse, Belgium).

2.2. Samples

Texicryl 13-031, a base emulsion, was obtained from Scott Bader. The sample was provided by Dr. T.J.S. Learner while at the Tate Gallery, London, UK.

2.3. Sample preparation

The Texicryl 13-031 base emulsion was painted out on aluminium foil and dried for two weeks. The dried sample was cut into small pieces (1–5 mm^2). About 500 μg of sample was transferred into a vial and extracted with 2 mL Milli-Q water for two weeks. The extract was transferred to a new vial and the water was evaporated under a stream of nitrogen.

2.4. MALDI-TOF-MS

For MALDI-TOF-MS analysis the residue recovered from the water extract (estimated 10–50 μg) was dissolved in ethanol. The amount of ethanol used roughly depended on the amount of residue. An aliquot of 4 μL of the solution was mixed with a 20 μL solution of 0.2 M 2,5-dihydroxybenzoic acid and 1 mM sodium iodide in ethanol. Sodium iodide was added to promote the formation of sodiated molecules during desorption and ionisation. An aliquot of 1 μL of the mixture was spotted on the MALDI target and dried at room temperature.

MALDI-MS was performed on a Bruker Biflex TOFMS (Bruker-Franzen Analytik GMBH, Bremen, Germany) and on a TofSpec 2E time-of-flight mass spectrometer (Micromass Limited, Wythenshawe, UK). The MALDI-MS systems were equipped with a nitrogen laser (337 nm). Spectra were obtained by averaging 50–100 spectra, with a typical laser fluency of about 5×10^{-3} J/mm^2 using the reflectron mode and a 20 kV acceleration voltage. Data were processed using the XMASS 5.0 software (Bruker Daltonik GMBH, Bremen, Germany) and MassLynx V3.5 software (Micromass Limited, Wythenshawe, UK).

2.5. Nano ESI-QTOF-MS

For nano ESI-QTOF-MS analysis the residue recovered from the water extract was redissolved in MeOH:H$_2$O (70:30). The sample was measured in the positive ion mode and in the negative mode. Ion exchange resin (Biorad, AG® 501-X8, 20–50 mesh) was added to the solution intended for positive ion mode analysis to remove all ions. All solutions were filtered over 0.2 μm Spinex Centrifugal Filters (Phenomenex, Torrance, USA) to remove particles that could block the spray needle. A final concentration of 10 mM NH$_4$Ac or 10 mM N(Bu)$_4$OH was used to enhance the ionisation process of the positive ion-mode and the negative ion-mode, respectively.

Nano ESI-QTOF-MS was performed on a Q-ToF2 instrument (Micromass Limited, Wythenshawe, UK). The solutions were sprayed with Econo10 needles or BG-10-58-2-CE-20 needles (New Objective, Woburn, USA) with a flow of approximately 10–80 nL/min.

2.6. Positive mode

Typical settings used in the positive mode are a capillary voltage of 0.7–2.0 kV, cone voltage of 0 V, collision energy of 10 eV, TOF voltage of 9.1 kV and the detector set at 2.1 kV. For nozzle skimmer dissociation (NSD) the cone voltage was adjusted to 60 V. Tandem MS (MSMS) analysis was performed with a collision energy of 20–60 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern. For NSD-MSMS analysis the cone voltage was set at 60 V, the collision energy at 20 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern.

2.7. Negative mode

Analysis in the negative ion-mode was performed with a capillary voltage of 0.7–1.5 kV, cone voltage of 10–30 V, collision energy of 10 eV, TOF voltage of 9.1 kV and the detector was set at 2.3 kV. MSMS analysis was performed with a collision energy of 20–50 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern.
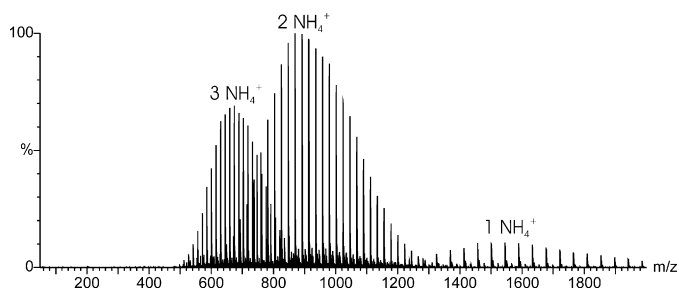
Fig. 1. ESI$^+$-MS spectrum of Triton X-405.

Fig. 3. ESI$^+$-NSD (cone voltage = 60 V) MS spectrum of Triton X-405.

Data were processed using the MassLynx V3.5 software (Micromass Limited, Wythenshawe, UK).

3. Results and discussion

3.1. MALDI-TOF-MS analysis of Triton X-405

MALDI-MS analysis was used to determine the MMD characteristics of Triton X-405 (C_8H_{17}-C_6H_4-$[OC_2H_4]_n$-OH) (spectrum not shown) and the M_r. The MMD was used to calculate the number-average molar mass (M_n), the weight-average molar mass (M_w) and the polydispersity (D) [22]. The values obtained are M_n = 1737 Da, M_w = 1769 Da and D = 1.02. Subtracting the sodium followed by n monomer masses from a cationized molecule yielded the M_r. The number of monomer masses which are subtracted equals the highest possible number without resulting in a negative number for the M_r. Nominal masses are used in this calculation, except for the monomer mass where a mass with a three decimal accuracy is used. The reasoning behind this is that using the monomer nominal mass for the calculation of M_r in polymers with high monomer numbers introduces a significant error. For example, a cationized molecule with a m/z = 1770 yields an M_r of 30 Da if a more exact monomer mass is used (M_r = 1770 − 23 − 39 × 44.026 = 30 Da) or an M_r of 31 Da if the nominal mass is used (M_r = 1770 − 23 − 39 × 44 = 30 Da), naturally the latter one is incorrect. Calculation of M_n, M_w and D of a MMD is the most common way of data reduction.

3.2. Nano ESI-QTOF-MS analysis of Triton X-405

The ESI-MS analysis was used to obtain information about the end-groups. Fig. 1 shows the nano ESI-QTOF-MS spectrum of Triton X-405. Mono (1+), double (2+) and triple (3+) ammoniated polymer molecules are observed in Fig. 1. The end-group information obtained is limited to the M_r. More specific end-group related information can, however, be generated by MSMS analysis.

The MSMS analysis on the mono (Fig. 2), doubly (not shown) and triply (not shown) charged polymer molecule (n = 38) shows two major fragment distributions. The most intense is the ion series 89 + 44n (marked with * in Fig. 2), which is characteristic
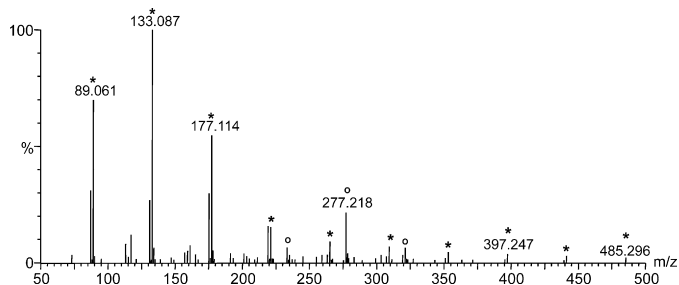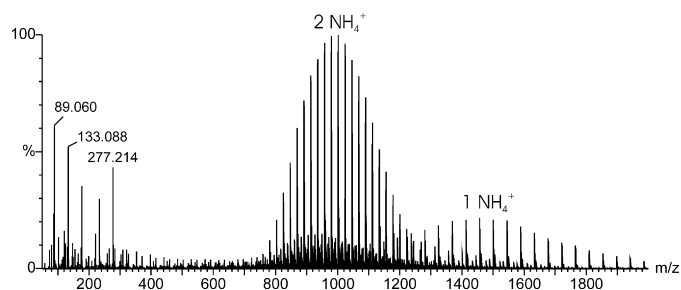
for the hydroxyl end-group (H-$[OC_2H_4]_{n+2}$$^+$). The presence of the octylphenyl end-group is suggested by the ion series 233 + 44.026n (1 ≤ n ≤ 3) as fragment ion distribution (marked with ○ in Fig. 2, C_8H_{17}-C_6H_4-$[OC_2H_4]_n$$^+$). An additional dissociation of the end-group containing ion-series would yield structural information, but our instrument is not equipped with MS^3 capabilities. As an alternative, nozzle skimmer dissociation (NSD) was used to produce the suitable precursor ions for tandem MS analysis.

Fig. 3 shows the NSD spectrum of Triton X-405. The main fragment distributions are similar to those observed in the MSMS analysis of the singly charged polymer molecule (Fig. 2). The m/z 233 of the octylphenyl containing fragment ion series was used as a precursor for tandem MS analysis. The resulting NSD-MSMS spectrum is depicted in Fig. 4 showing a fingerprint of the octylphenyl end-group. This fingerprint was used for a full identification of PEG compounds with an octylphenyl end-group found in the water extracts of the acrylic films.

3.3. MALDI-TOF-MS analysis of Texicryl 13-031

Three PEG compound distributions were observed in the MALDI-MS spectrum of Texicryl 13-031 (Fig. 5). The first PEG (*) has a M_w = 645, M_n = 628, D = 1.03 and M_r = 0 Da. The second PEG (−) has a M_w = 770, M_n = 746, D = 1.03 and M_r = 14 Da. And the third PEG (○) has a M_w = 871, M_n = 854, D = 1.02 and M_r = 28 Da. In addition the relative estimated abundance (X) of each PEG compound in the spectrum was calculated by $X = \Sigma(m_i N_i)$, where N_i represents the number of polymer molecules with mass m_i. Subsequently the percentage of the summed relative estimated abundance in the spectrum was calculated for each MMD resulting in M_w = 645 → 11%, M_w = 770 → 55% and M_w = 871 → 34% for Texicryl 13-031.

3.4. Nano ESI-QTOF-MS analysis of Texicryl 13-031 in the positive mode

The ESI-MS analysis of Texicryl 13-031 (Fig. 6a) shows a more complex pattern than the three distributions observed in the MALDI spectrum. A representative detail of the multiple distributions is

Fig. 2. ESI$^+$-MSMS (collision energy = 60 eV) spectrum of m/z 1897 observed in the Triton X-405 ESI$^+$-MS spectrum (m/z 50–500 region is shown).
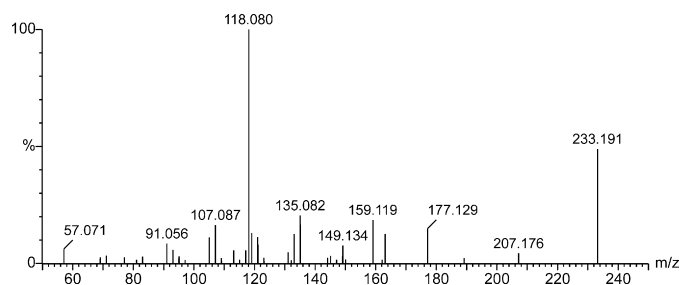

Fig. 4. ESI$^+$-NSD (cone voltage = 60 V) MSMS of m/z 233 (collision energy = 20 eV) spectrum of Triton X-405.
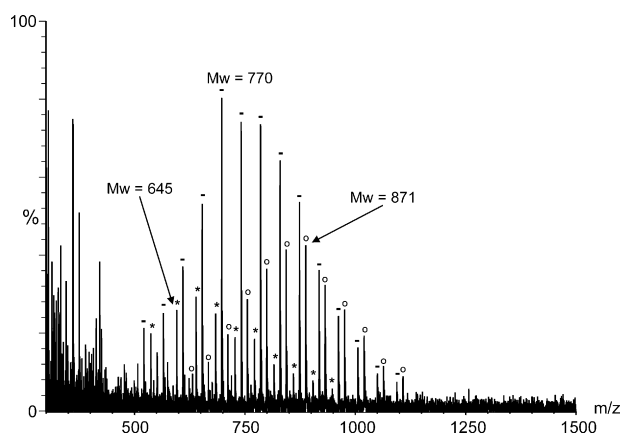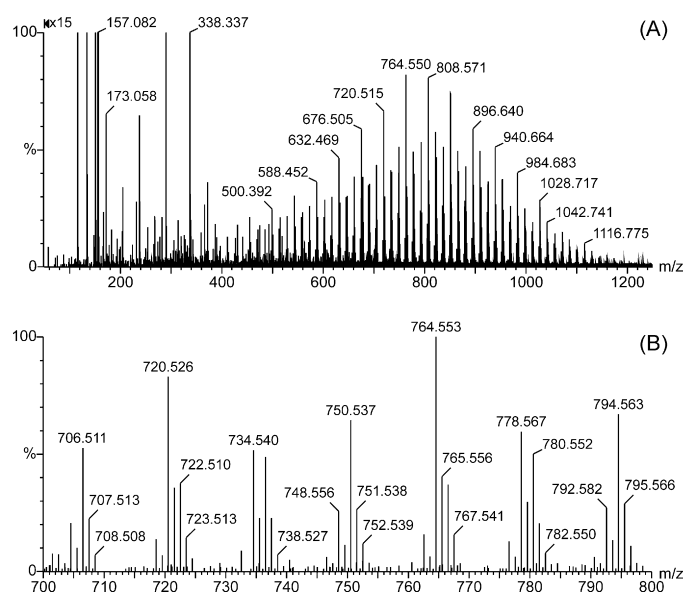
Fig. 5. MALDI-MS spectrum of Texicryl 13-031.

Fig. 6. (a) ESI$^+$-MS spectrum of Texicryl 13-031. (b) ESI$^+$-MS spectrum (m/z 700–800) of Texicryl 13-031.

depicted in Fig. 6b. MSMS analysis was performed on m/z 722, m/z 736, m/z 750, m/z 764 and m/z 778 for structural identification.

The MSMS analysis of m/z 722 (not shown) gives two major fragment ion series at $89 + 44.026n$ and $247 + 44.026n$. The $89 + 44.026n$ fragment ion series represents the H-$[OC_2H_4]_{2+n}$ fragment. The NSD-MSMS fingerprint spectrum of m/z 247 (not shown) was similar to those of the reference PEG compounds (Triton N-57, Tergitol NP-9 and Tergitol NP-40 (not shown)), which all contain PEG compounds with a nonylphenyl end-group. The M_r of 0 Da corresponds with the PEG compound at $M_w = 645$ Da observed in the MALDI-MS spectrum (Fig. 5). With the aid of reference PEG compounds, the nonylphenyl end-group could be unambiguously identified.

Table 2
Assignment of structures to the $C_{10}H_{21}$ end-group containing fragments.

m/z selected for MSMS	Observed fragments				
	0	1		2	
	m/z	m/z	Monomer	m/z	Monomer
736.523	141.160	199.207	PO	257.246	PO
750.540	141.162	185.200	EO		
764.554	141.162	199.205	PO	243.227	EO
778.570	141.162	199.204	PO	257.246	PO

The identification of the major fragment distributions of the MSMS spectra of m/z 736, 750, 764 and 778 was more complex than m/z 722. The MSMS data suggest that the polymeric part contains more than one type of monomer and that there is variation in the mass of the end-groups.

One of the fragment ion series seen in all MSMS spectra of m/z 736, 750, 764 and 778 is $91 + 44.026n$ ($0 \le n \le 4$). The accurate mass of m/z 91 suggests an elemental composition of C_7H_7. The structure of the fragment ion series is proposed to be C_7H_7-$[OC_2H_4]_n^+$ (benzyl). Other fragment ion distributions start at m/z 113 (Table 1) and 141 (Table 2) are thought to contain PO and EO monomers. The structures of these ions are thought to correspond to C_8H_{17}-$[OC_3H_6]_n$-$[OC_2H_4]_m^+$ and $C_{10}H_{21}$-$[OC_3H_6]_n$-$[OC_2H_4]_m^+$ for the octyl and decyl end-groups, respectively. The decyl end-group fragments observed for m/z 736 are low in intensity and are thought to originate from the +2 isotope peak of m/z 734. The observed complex pattern observed in the ESI-MS spectrum is therefore proposed to be an EO/PO block copolymer in combination with octyl and decyl end-groups. The copolymeric structure of the molecules analysed with MSMS analysis, for both end-groups, are shown in Table 3.

The PEG compounds with a $M_w = 770$ and 871 Da are not observed with ESI-MS in the positive mode. These PEG compounds may contain anionic groups and are therefore not observed since an ion exchange resin was used to remove interfering cations and anions. In the negative mode the anionic PEG compounds remained in the sample extract because an ion exchange resin was not necessary and therefore not used.
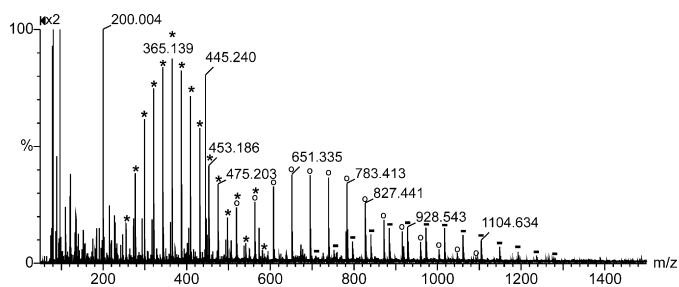
3.5. Nano ESI-QTOF-MS analysis of Texicryl 13-031 in the negative mode

Tetrabutyl ammonium hydroxide was added to the samples for the ESI-MS analysis in the negative mode to enhance negative ionisation. PEG compounds with acidic end-groups are deprotonated by the hydroxide and are observed as negative ions.

The ESI-MS analysis of Texicryl 13-031 in the negative mode (Fig. 7) shows one doubly (*) and two singly charged (○ and –) ion distributions. The singly charged distribution (○) has a residual end-group mass of 36 Dalton ($651 + 1$ (H$^+$) $- 14 \times 44 = 36$ Da). A PEG compound with $M_r = 36$ is, however, not observed with MALDI-MS analysis. MALDI-MS analysis did show a PEG compound with a $M_r = 14$ Da which differs 22 Dalton with the observed $M_r = 36$ Da. The difference indicates that the acidic group of the poly-

Table 1
Assignment of structures to the C_8H_{17} end-group containing fragments.

m/z selected for MSMS	Observed fragments						
	0	1		2		3	
	m/z	m/z	Monomer	m/z	Monomer	m/z	Monomer
736.523	113.132	171.173	PO	215.200	EO		
750.540	113.132	171.173	PO	229.215	PO	273.241	EO
764.554	113.131	171.173	PO	229.215	PO	287.259	PO
778.570	113.132	171.173	PO	229.215	PO	287.255	PO

Table 3
The proposed complete block copolymeric structures and end-group assignment for the polymer ions selected for the ESI$^+$-MSMS analysis.

m/z	C8H17O-[PO]$_n$-[EO]$_m$-C$_7$H$_7$			C10H21O-[PO]$_n$-[ED]$_m$-C$_7$H$_7$			Calculated mass (+NH$_4^+$)
	n		m	n		m	
736.523	1		10	–		–	736.521
750.540	2		9	0		11	750.537
764.554	3		8	1		10	764.552
778.570	4		7	2		9	778.568

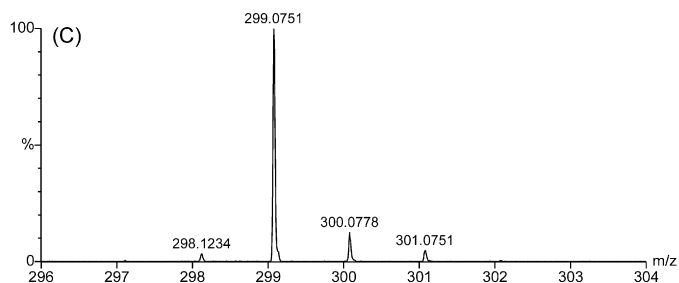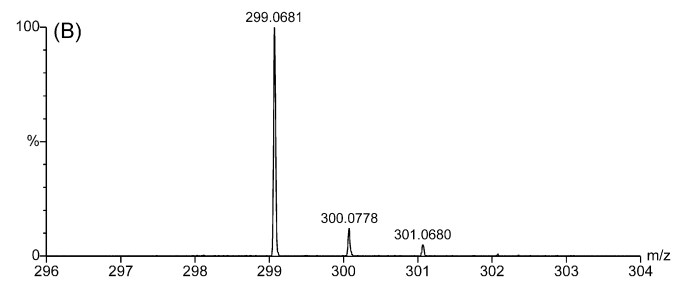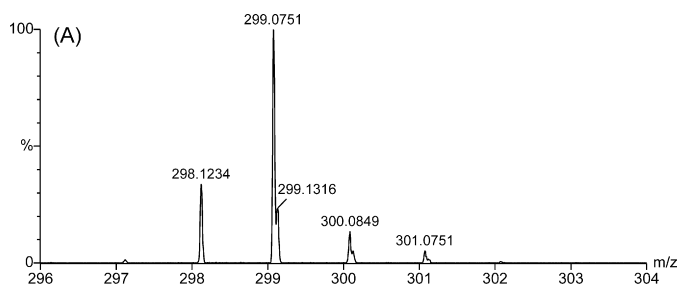

Fig. 7. ESI$^-$-MS spectrum of Texicryl 13-031.

mer molecule was present as a sodium salt instead of an acid (23 (Na$^+$) − 1 (H$^+$) = 22 Da) in MALDI analysis.

The doubly charged (*) and the singly charged ion distribution (−), observed in Fig. 7, originate from one distribution. The doubly charged distribution of ions lost 2 protons, whereas for the singly charged polymer molecule one of the two negative charges is compensated by the tetrabutyl ammonium cation ((m/z 972−242 (N(Bu)$_4$)$^+$)/2 = m/z 365). The calculated M_r for both distributions is therefore 28 Da and thus correspond to the MMD observed in the MALDI-MS spectrum at M_w = 871 (Fig. 5).

The MSMS analysis of m/z 365 (Fig. 8) show the fragment distribution 123 + 44n (*). Proposed to be CH$_2$=CH-[OC$_2$H$_4$]$_n$-SO$_4^-$ (0 ≤ n ≤ 7), suggesting that a sulphate group is one of the end-groups of the polymer molecule. MSMS analysis of polyethylene glycol 600 sulphate (not shown) was used to confirm the presence of the sulphate end-group since similar fragment distributions and isotope patterns were observed. The other end-group only gives one peak at m/z 298 (Fig. 9a), thought to be: C$_9$H$_{19}$-C$_6$H$_3$(SO$_3^-$)-O·. Unfortunately our instrument is not able to perform MS^3 analysis to unambiguously confirm the structure. The intact polymer molecule is proposed to be: C$_9$H$_{19}$-C$_6$H$_3$(SO$_3^-$)-[OC$_2$H$_4$]$_n$-SO$_4^-$.

The MSMS analysis of the singly charged ion distribution (○) at m/z 651 plus its isotopes (Fig. 10) also shows the 123 + 44n fragment distribution (*) inclining that the sulphate group is one of the end-groups of the polymer molecule. The other end-group is observed as a loss of 220 Da (m/z 651−431) and as a small peak at m/z 219, suggesting the loss of a nonylphenol end-group and presence of nonylphenolate, respectively. The PEG compound with M_r = 14 seems to contain a nonylphenyl end-group on one side and a sulphate group on the other end of the polymer molecule.

Fig. 9. (a) Texicryl 13-031 ESI$^-$-MSMS spectrum of m/z 365 (collision energy = 25 eV, m/z 296–304 region is shown). (b) Texicryl 13-002 ESI$^-$-MSMS spectrum of m/z 651 (collision energy = 50 eV, m/z 296–304 region is shown). (c) Texicryl 13-031 ESI$^-$-MSMS spectrum of m/z 651 (collision energy = 50 eV, m/z 296–304 region is shown).

There are, however, indications that there are two isomers present in the M_r = 14 Da MMD of Texicryl 13-031. A closer look at the m/z 296–304 region of the m/z 365 (Fig. 9a) and m/z 651 (Fig. 9b) MSMS spectra of Texicryl 13-031 and the m/z 651 spectrum of Texicryl 13-002 (Fig. 9c) shows some small differences. In the Texicryl 13-031 spectrum a small peak at 298 suggests that the m/z 651 is in

Fig. 8. Texicryl 13-031 ESI$^-$-MSMS spectrum of m/z 365 (collision energy = 25 eV).
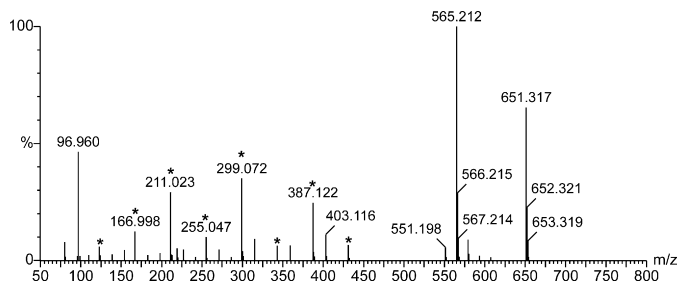
Fig. 10. Texicryl 13-031 ESI$^-$-MSMS spectrum of m/z 651 (collision energy = 50 eV).

fact a mixture of two isomers whereas only one PEG compound is present in Texicryl 13-002, which is C_9H_{19}-C_6H_4-$[OC_2H_4]_n$-SO_4^-). The small peak at m/z 298 is indicative for the structure proposed as C_9H_{19}-$C_6H_3(SO_3^-)$-$O\cdot$, a sulfonic group attached to the phenyl group. The structures of the two isomers that represent the MMD with $M_r = 14$ are therefore: C_9H_{19}-$C_6H_3(SO_3^-)$-$[OC_2H_4]_n$-OH and C_9H_{19}-C_6H_4-$[OC_2H_4]_n$-SO_4^-.

The methodology developed illustrates that a combination of MALDIMS, ESIMS and ESIMSMS gives a complete molecular analysis of the water extractables in acrylic medium. Further application to base and modified emulsions, liquid paints, dried paints, samples from a palette and paint microsamples from paintings [21] demonstrates that the complexity of the composition of artists' paints requires this approach because a wide range of PEGs with different end-groups is encountered in acrylic paint formulations. The presented methodology is able to detect and characterise PEG surfactants with sulphated end-groups which can present special conservation challenges.

4. Conclusions

The combined application of MALDI and nano ESI mass spectrometry to the characterisation of synthetic acrylic paint media allows the determination of the MMDs and the characterisation of the end-groups of the PEG surfactants found in minute volumes of water extracts. The methodology is also suitable for detection of sulphated end groups. A polymeric compound different from PEG found in the water extract of a Texicryl 13-031 base emulsion could be identified as a PPG/PEG block copolymer.

Acknowledgements

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