UTILIZATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOR STUDY OF CHEMICAL AND MOLECULAR STRUCTURE OF SELECTED PAINT MATERIALS

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Abstract

The aim of this work is the characterization of selected new and traditional materials used in paint applications using various techniques of liquid chromatography. These techniques are high performance liquid chromatography coupled with mass spectrometry (LC-MS), gel permeation chromatography (GPC) and GPC in combination with a multi-angle light scattering detector and an online viscometer (GPC-MALS-VIS). Analyzed materials were polyglycidol, bisphenol A, epoxy resins based on bisphenol A and star polyesters based on lactide and caprolactone.

Introduction

Polyglycidol is a relatively new material characteristic of high functionality and thus very good reactivity. For this reason, we studied the structure in connection with the possible use in paint applications. A derivatization of polyglycidol by phenylisocyanate to give urethanes was used for the analysis by GPC and comparison with mass spectrometry [1-4].

Bisphenol A is the raw material for synthesis of epoxy resins of varied molar mass and applications. Impurities in this material can impact the composition and quality of epoxy resins based on bisphenol A. With regard to the wide area of applications of these substances it is necessary to keep the pace with constantly evolving instrumentation and apply it in addition to new materials on traditional ones, for their comparison. Side reactions leading to various side products may take place during the synthesis of bisphenol A. Various chromatographic methods, including liquid chromatography in combination with diode array detector (LC-DAD), have been utilized in identification of these side components in bisphenol A yet. This work focuses on the possibility of using mass spectrometry for analysis of this material, specifically using electrospray ionization. In addition to the analysis of bisphenol A, epoxy resins based on bisphenol A were also analyzed regarding corresponding minor components[5-8].

Other interesting materials for paint applications, which were characterized, are star polyesters based on lactide and caprolactone with different number of arms and different molar mass. Polyesters are intended for various applications in paint industry. Corresponding linear analogues were analyzed too. Trimethylolpropane was used as the center of star for three armed stars, pentaerythritol was used for four armed stars and dipentaerythritol was used for six armed stars. The compound for linear analogues was 1,4-butandiole[9-10].

Results and discussion

First analysis of polyglycidol was performed using mass spectrometry with suitable ionization conditions. This is shown in Figure 1.

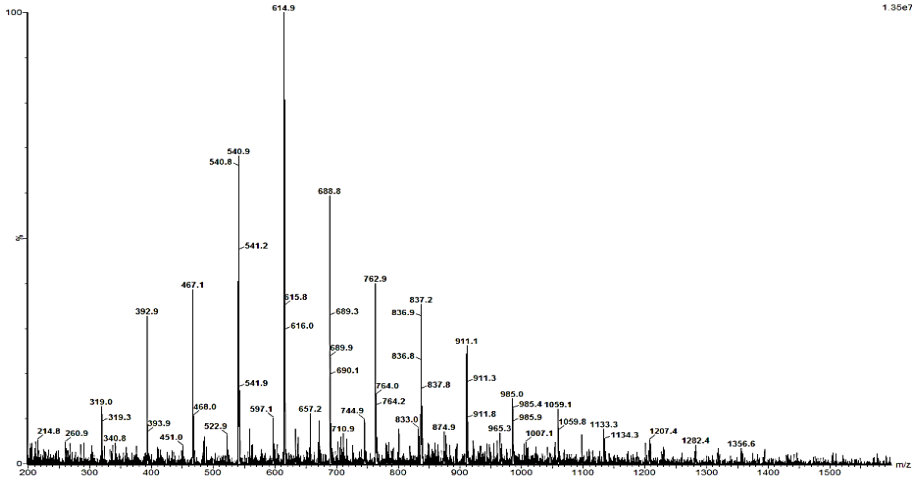

Figure 1. MS spectrum of polyglycidol in positive electrospray ionization mode

Individual oligomers up to a polymerization degree around twenty with a top of distribution at polymerization degree of eight can be identified in mass spectrum. The derivatization of polyglycidol by phenylisocyanate to give urethanes was used for analysis by GPC and comparison with mass spectrometry. The derivatization was performed in order to make polyglycidol soluble in a common GPC solvent, i.e. tetrahydrofuran. Five determinations was performed for five different derivatizations. Corresponding averages of molar mass, i.e. number-average (M_n), weight-average (M_w) and z-average (M_z) were determined. Results showed that the derivatization of polyglycidol is well reproducible. The top of the distribution around the polymerization degree of eleven was calculated from data obtained by GPC. MS and GPC data revealed, that polyglycidol is oligomeric compound with polymerization degree in range of several units to several tens with the top of the distribution around the polymerization degree of ten.

Bisphenol A was another analyzed material. First analysis was performed using mass spectrometry. This is shown in Figure 2. Suitable ionization conditions were selected. These conditions were subsequently used for the analysis by LC-MS.

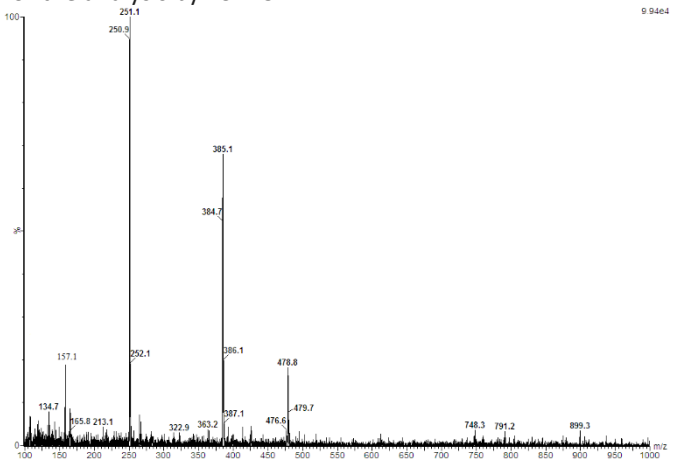

Figure 2. MS spectrum of bisphenol A

The most intense ion in the mass spectrum at m/z = 251 belongs to sodium adduct $[M+Na]^+$ of bisphenol A. Firstly LC-MS analysis of bisphenol A was performed. Thereafter LC-DAD analysis at 280 nm was performed also for their comparison. Following components were detected in the sample: 4-isopropenylphenol, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 2,4-dihydroxy-2,2-difenylpropane and 2,4-bis(4-hydroxycumyl)phenol (trisphenol). Fractions of major and minor components above-mentioned was calculated as relative areas of UV peaks: 0.1, 94.4, 3.9 and 0.6 %, respectively. The remaining 1.0 % belongs to unidentified compound with the molar mass 456.

Epoxy resins based on bisphenol A were also analyzed regarding corresponding minor components. First analysis was performed using mass spectrometry to select suitable ionization conditions for LC-MS. Fig. 3 A shows the spectrum obtained in optimum ionization conditions, when the monomer of diglycidyl ether of bisphenol A (DGEBA) has higher intensity and Fig. 3 B shows the spectrum in ionization conditions, when the dimer and the trimer of DGEBA have higher intensity. Then LC-MS analysis was carried in these ionization conditions.

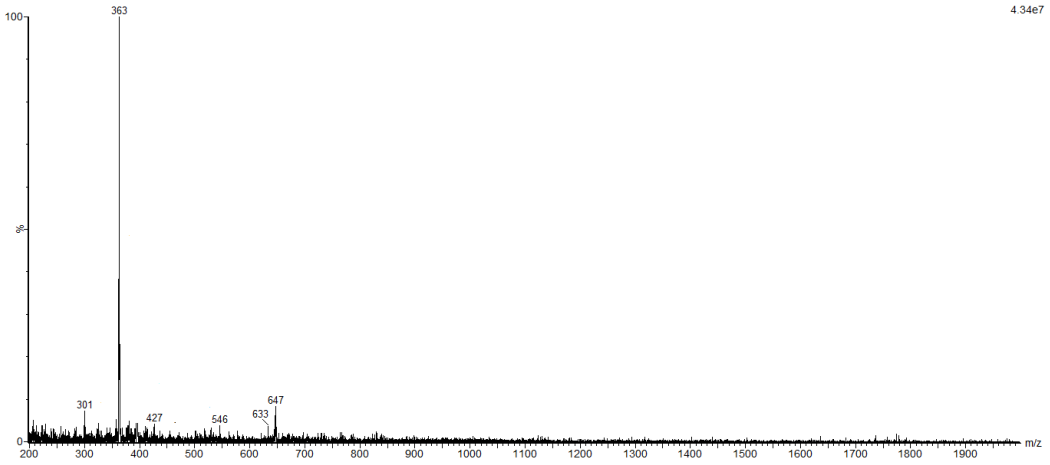

Figure 3 A. MS spectrum of monomer

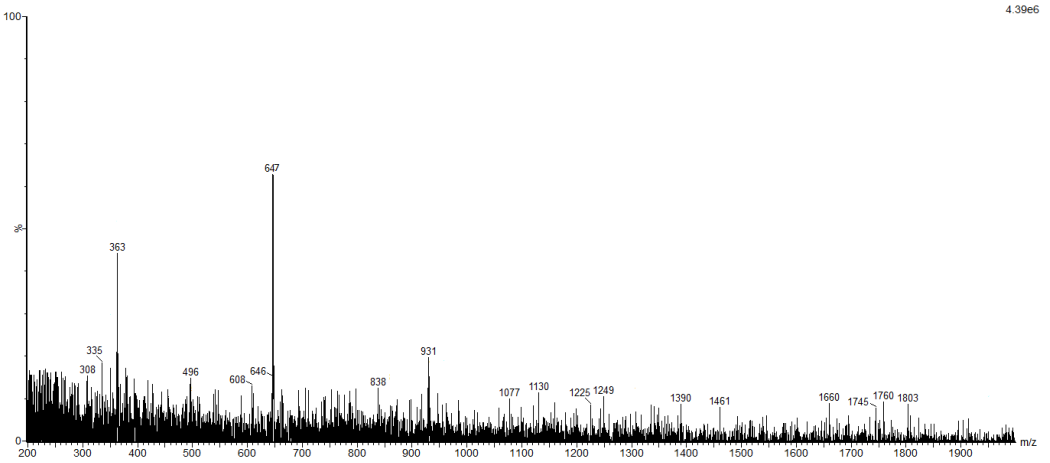

Figure 3 B. MS spectrum of dimer and trimer

Ratios m/z of each analyzed epoxy oligomers and the most common adducts, which can be observed in spectra are shown in Table I.

Table I

Ratios *m/z* of epoxy oligomers and the most common adducts

Oligomer	*m/z*	$[M + NH_4]^+$	$[M + Na]^+$	$[M + K]^+$
Monomer	340	358	363	379
Dimer	624	642	647	663
Trimer	908	926	931	947

The minor peak, which was eluted before monomer of DGEBA in LC-MS chromatogram, showed ions $[M+NH_4]^+$, $[M+Na]^+$ and $[M+K]^+$ and the corresponding molar mass was 358, i.e. 18 units more than the molar mass of monomer of DGEBA. The peak was identified as DGEBA with one epoxy group open by addition of water. Analogously, this was observed also at the dimer and at the trimer. Obtained data showed, that the commercial product CHS EPOXY 530 contained very few impurities, in contrast to some papers that identified significantly more impurities at higher concentrations. Relative areas of oligomers in chromatogram of CHS EPOXY 530 was about 82.5, 8.0, 0.9 % for monomer, dimer and trimer, respectively. The relative area of α-glycol of DGEBA was approximately 0.7 %. More than 7.0 % included peaks immediately before individual oligomers. They arised from the dissolution of the sample in methanol. They are likely products of addition of methanol on epoxy group. Consequently, it is better to dissolve samples in tetrahydrofuran.

Other materials, which were characterized, are star polyesters based on lactide and caprolactone with different number of arms and different molar mass. GPC-MALS was used for the characterization of polyesters in sense of molar mass distribution and number of arms. This stars were theoretically containing three, four and six arms. Corresponding linear analogues were analyzed as well in different ratio of lactide and caprolactone. Characteristics of selected three armed stars are listed in Table II.

Table II

Resulting characteristics of selected three armed star polyesters based on lactide and caprolactone

Sample	Lactide/Caprolactone	M_n [g mol^{-1}]	M_w [g mol^{-1}]	M_z [g mol^{-1}]	M_w / M_n
H 13	1/2	1300	1480	1690	1,14
H 14	1/3	1630	1900	2200	1,17
H 15	1/4	1910	2190	2470	1,15
H 16	1/5	2370	2650	2950	1,11
H 17	1/6	2680	2990	3320	1,11
H 18	2/5	2750	3140	3550	1,14
H 19	2/6	3030	3560	4180	1,18
H 20	2/8	3730	4280	4920	1,15

It can be seen from Table II that the molar mass increases with increasing content of caprolactone. The suitability of GPC-MALS for the determination of molar mass distribution of oligomers with lower molar mass will be verified by comparison with results of mass spectrometry. Additionally, constants of Mark-Houwink equation for linear polyesters of different ratio lactide/caprolactone were determined in order to characterize the degree of branching of star polyesters. The specific refractive increment of polyesters of different ratio lactide/caprolactone was determined as an important physical quantity needed for accurate processing MALS data.

Conclusion

GPC after the derivatization of polyglycidol allows the characterization of molar mass distribution. LC-MS can be used for detailed identification of major and minor components of bisphenol A and epoxy resins based on bisphenol A. GPC-MALS provides valuable information about the molar mass distribution of star polyesters based on lactide and caprolactone.

Acknowledgement

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