

*Dedicated to the memory of  
Professor Cristofor I. Simionescu (1920–2007)*

## CHARACTERIZATION OF SOME POLYSILOXANES CONTAINING NUCLEOBASES AND AZOBENZENE GROUPS IN THEIR SIDE-CHAIN OR CROWN AZO-ETHER WITHIN POLYMERIC CHAINS BY MEANS OF NEGATIVE-IONIZATION MASS SPECTROMETRY WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION

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Some polysiloxanes containing azobenzene and nucleobase groups (adenine, thymine, cytosine), or crown azo-ether 18C6 within polymeric chains, were characterized by means of mass-spectrometry with atmospheric pressure chemical ionization and fluorescence spectra. The mass spectral acquisition was limited to 2000 Da, with an ion resolution up to  $\pm 2$  Da. The fragmentation of the polymer molecules was possible by combined degradations due to both polymeric chain and group scissions. MS-MS spectra were studied in some circumstances by collisional induced fragmentation of selected negative pattern ions.

### INTRODUCTION

Due to the reorganization process at nanometric scale under UV/VIS irradiation, azo-containing polymers have attracted much attention as materials with applications in biology, optoelectronics and nano-manipulation field.<sup>1-4</sup> Responsible for this behaviour is the *trans-cis* isomerization of the azo-groups, connected in the polymeric main- or side-chain. Recent studies of Karageorgiev *et al.*<sup>3</sup> concerning the possibility to generate a directional flow on the surface of an azo-polymeric film (if a polarized UV laser source is used) open a new interesting research direction directly related to the biomolecules nano-manipulation. For these purpose azo-polymers containing nucleobases in the side-chain were synthesized.<sup>5</sup> The potential interest in the field of molecules nano-manipulation is due to the directional flowing

capacity of the azo-materials, when a polarised UV laser source irradiation is used. But due to the presence of the nucleobases and azobenzene groups in the polymeric chain, capable to generate specifically interaction with the solvents or the organic molecules, this class of materials can be attractive, too, for different chromatographic techniques.

During the last decades, mass spectrometry has been extensively used in polymer studies in order to provide information about oligomer distributions, average molecular weights and fingerprint patterns for their identification, monomeric unit sequences, branching, cross-linking or other side-chain substitution, copolymer structures, as well as the presence of additives or impurities in polymer matrix. However, in spite of the importance of polysiloxane based materials in obtaining stationary phases in gas or liquid

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chromatography, MS studies have been rarely focused on polymers containing a siloxane structure. For instance, characterization of polydimethylsiloxane, polyhydroxymethylsiloxane, and polymethylphenylsiloxane was achieved by means of time-of-flight secondary ion mass spectrometry in order to investigate effects of functional group changes on polymer fragmentation mechanisms.<sup>6</sup> An in-situ mass spectrometry study on low weight (up to 300 amu) has also been reported for studying the fragmentation of linear and cyclic siloxanes in a glow discharge compared with ex-situ FTIR analyses of deposits.<sup>7</sup> The aim of this work is to study some polysiloxanes containing nucleobases and azobenzenic groups in their side-chains, or crown azo-ether 18C6 within polymeric chains, by means of negative-ionization mass-spectrometry with atmospheric pressure chemical ionization (APCI) and the influence of different substitution groups on the MS fragmentation processes. This analytical technique is known as a modern detector in liquid chromatography, which is applicable to the determination and structural confirmation of a wide range of polar and nonpolar compounds from complex samples, *e.g.*<sup>8-12</sup>

## EXPERIMENTAL

The acquisition of MS spectra was performed with the aid of the ion trap mass spectrometer (G24450), with atmospheric pressure chemical ionization (APCI), used as an off-line configuration of a liquid chromatographic system (HPLC). System control and data acquisition were made with the Agilent LC/MSD trap software version 4.2, integrating the MSD Trap Control software version 10.02 from Brucker Daltronics. The parameters controlling the APCI-MS interface were following: drying gas (N<sub>2</sub>) temperature: 300°C; vaporizer temperature: 350°C; drying gas flow: 10 mL/min; pressure of the nebulizer gas: 60 psi; capillary voltage: 4500 V; corona discharge: 5000 V. The detection of negative ions was achieved for the spectral domain up to 2000 Da with ion resolution set up to ±2 Da.

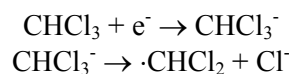
A concentration of about 1000 µg/mL substance in chloroform was used in all experiments for their APCI-MS characterization.

## RESULTS AND DISCUSSION

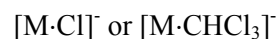
The possibility to obtain azopolysiloxanes modified with nucleobases (adenine and thymine) with potential application in immobilization and nanomanipulation of biomolecules has been described in a recent paper.<sup>5</sup> A photo-fluidization

mechanism based on the concept of the conformational instability was proposed, which can explain the presence of the fluid state below the glass transition. The azopolymers were previously characterized by <sup>1</sup>H NMR, GPC, DSC, DTG, UV spectroscopy, AFM analysis, and molecular simulations. Depending on the type of nucleobase used, the surface of the azopolysiloxane film can be structured in different ways under UV irradiation. Photoisomerization studies in solid state were carried out to demonstrate the influence of the operational conditions (presence or absence of natural visible light) on the polymeric film UV response. Details concerning the polymers synthesis according to the scheme given in Fig.1 and their characterization were previously reported.<sup>13-15</sup>

In atmospheric pressure chemical ionization the liquid sample is sprayed through a heated vaporizer at atmospheric pressure. The resulting gas-phase solvent molecules are then ionized by means of electrons discharged from a corona needle. Thus, the solvent ions will transfer charge to the analyte molecules through chemical reactions, known as chemical ionization. In case of using chloroform as sample solvent, due to the high electronegative character of the three chlorine atoms, the fragmentation process may be initiated by one of the following processes:



In such case, the adducts formed during fragmentation process can be identified as following species:



having the following mass values: (M + 35); (M + 37), and, (M + 118); (M + 120); (M + 122); (M + 124), which are not possible to be detected in the low mass domain, excepting one experiment.

Two main types of fragmentations are possible to occur in polymeric polymeric molecules subjected to MS process. One type occurs by simple elimination of different groups in side-chain, which can be seen in MS spectrum at lower values of *m/z* (up to 350 u.a.m.). On the other hand, more complex fragmentation based on scissions of Si-O bond in polysiloxane chains and fragment transpositions can be seen at higher values of *m/z*. The result of Si-O bond scissions were in many cases a strong background with multiple signals up to the highest studied *m/z* interval.

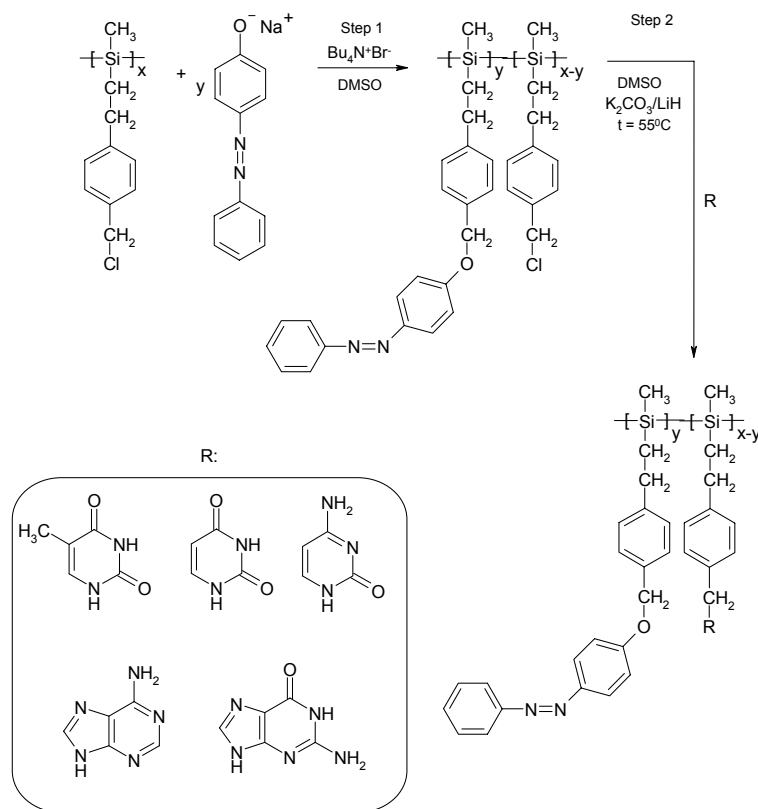


Fig. 1 – Synthesis schema of polysiloxanes containing nucleobases or azobenzene groups in their side-chain.

The MS spectrum of polysiloxane modified with only azobenzene is given in the next figure.

Its spectrum revealed four major spectral lines, situated at  $m/z = 197$ ; 1214; 1350 and 1533.

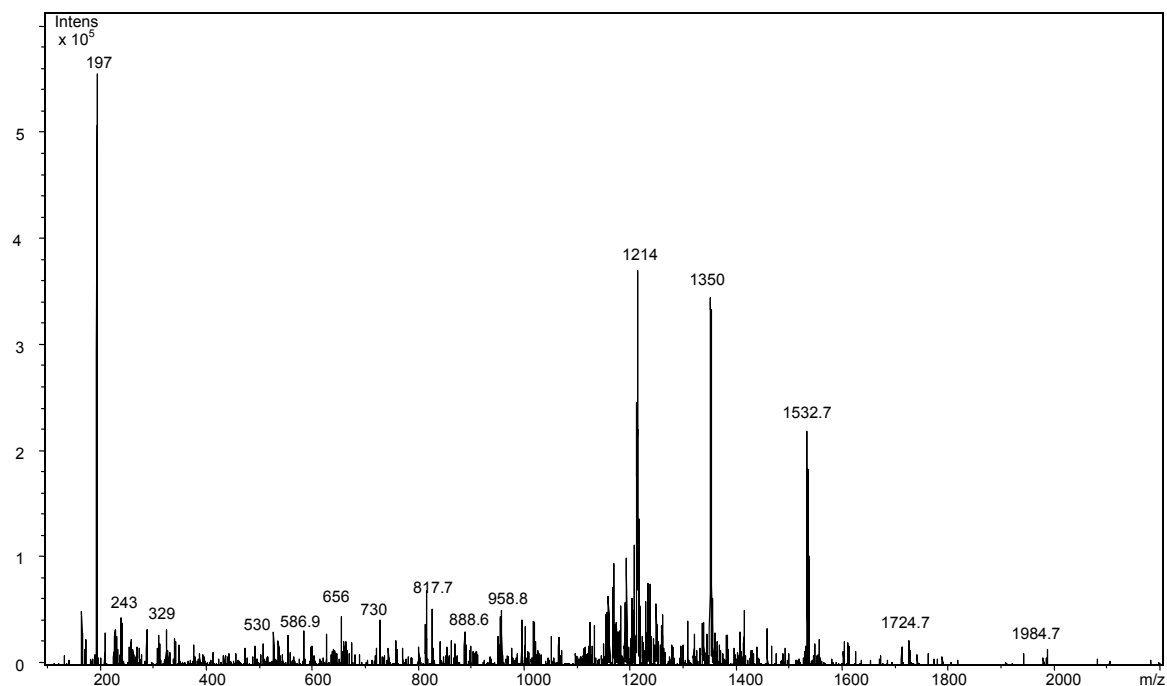
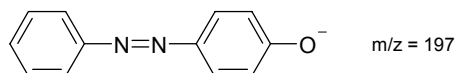
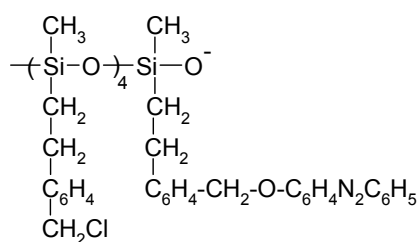


Fig. 2 – Mass spectrum of the polysiloxanes modified with azobenzene.

Spectral line at  $m/z = 197$  is assigned to a cleavage between C and O from the azobenzene group, which were characteristics to all polymers containing this functional group. The resulting fragment has the following structure:



The signal situated at  $m/z = 1214$  is assigned to the dimerization of the species having both radical and anionic characters:

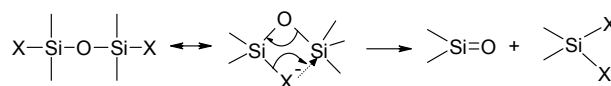


Such event is likely to take place if we take into account the large number of oligomer species obtained soon after ionization process. Thus, this dimeric fragment is characterized by a charge of 2.

The other fragments having  $m/z = 1214$ ; 1350 and 1532 could be assigned by solving the mathematical equations:  $212x + 374y = m/z$ ,  $x$  and  $y$  being explained in Fig. 1. One condition for these equations is  $x$  and  $y$  to be whole numbers. However, taking into account the errors

encountered in spectrum recording due to the poor spectral resolution approximate whole numbers are also desirable in spectral line assignments. Thus, spectral line at  $m/z = 1350$  was assigned to the fragment composed from 1 monomer of chlorobenzyl and 3 monomeric groups of azobenzene.

One possible transposition-based fragmentation mechanism, already proposed for other similar siloxane based structures,<sup>16</sup> is likely to take place simultaneously to chain scissions:



When chlorine atom from polysiloxane was substituted with adenine only, the MS spectrum became extremely complicated, as can be seen in Fig. 3.

Surprisingly, the MS spectrum of polysiloxane modified with azobenzene and adenine was simpler and characterized by five spectral lines, which have been very distinguishable from the background signal, as can be seen from the next figure. This time, these signals can be more easily interpreted according to the polymer structure (below Fig. 4).

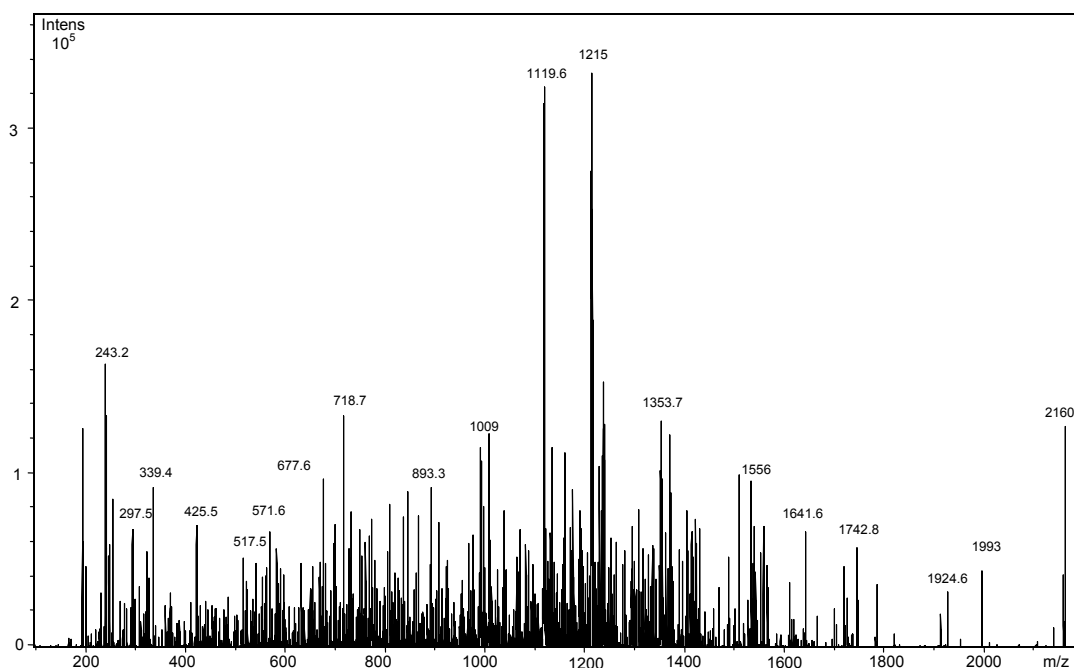


Fig. 3 – MS spectrum of polysiloxane modified with adenine.

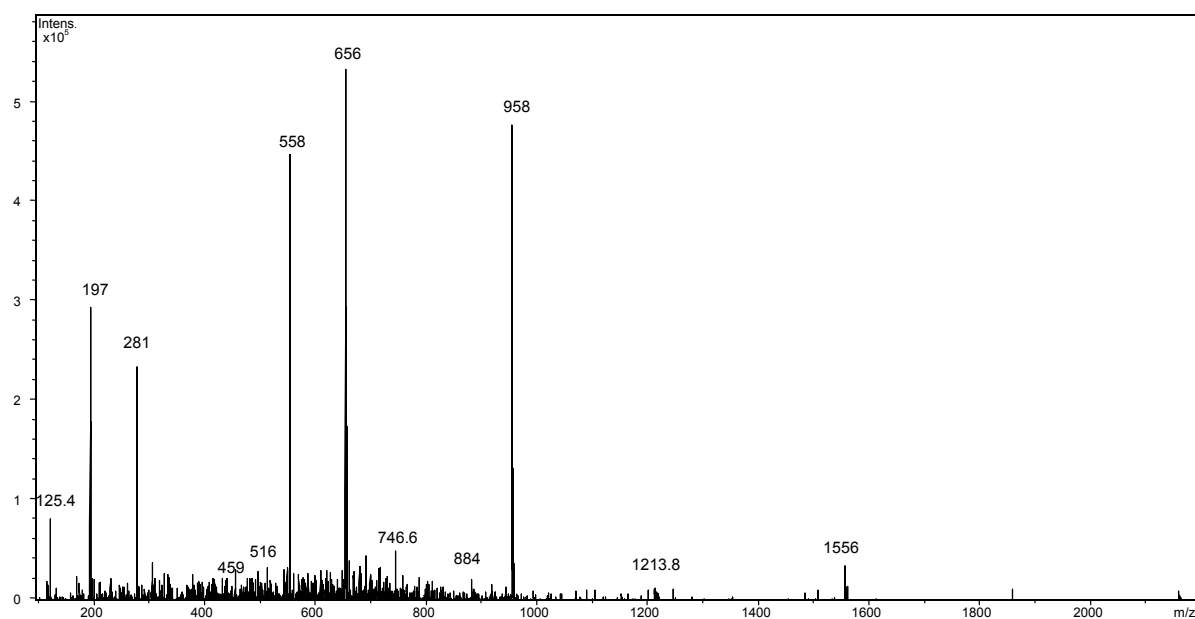


Fig. 4 – MS spectrum of polysiloxane modified with azobenzene and adenine.

Spectral line situated at  $m/z = 656$  can be assigned to the adduct between  $\text{Cl}^-$  and 2 monomer units ( $M_{\text{monomer}} = 311$ ); the corresponding double line corresponds to the two isotopes of chlorine and their isotopic abundance. Spectral line situated at  $m/z = 558$  can be explained by formation of a fragment adduct between  $\text{Cl}^-$  and one monomer unit of 212 a.m.u. and one monomer unit of 311 a.m.u.

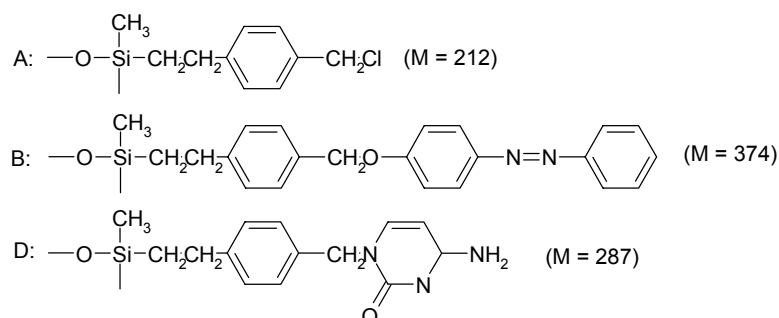
Spectral line at 956 is due to the formation of a fragment adduct between  $\text{Cl}^-$  and three monomer units of 311 a.m.u., simultaneously with one C loss. Two monomer units of 374 u.m.a. are identified as spectral line situated at  $m/z = 747$ , which may be a result of a hydrogen elimination with the aid of chloride ion. Three units of 311 u.a.m. and one chloride ion explain the formation of spectral line situated at  $m/z = 958$ .

In all these cases cyclic fragments are also likely to result from fragmentation processes, and previously reported in some other applications.<sup>6</sup>

The mass spectrum of polysiloxane derivatized with citosine or thymine only have the similar

feature as that discussed in case of adenine modified polysiloxane MS spectrum: no spectral line are very distinguishable from the background signal and therefore no distinct fragmentation is observable. For instance, the APCIMS spectrum of polysiloxane modified with thymine groups is given in Fig. 5.

The same tendency was observed at siloxane polymers modified with azobenzene and citosine or thymine as mentioned in case of polysiloxane modified with azobenzene and adenine. However, the mass spectrum in case of polysiloxane modified with azobenzene and citosine was somehow simpler than that obtained for polysiloxane modified with azobenzene and thymine. In this case, for the identification of fragmentation type in siloxane polymer modified with azobenzene and citosine (Fig. 6) the fragment mass of following monomeric groups were calculated:



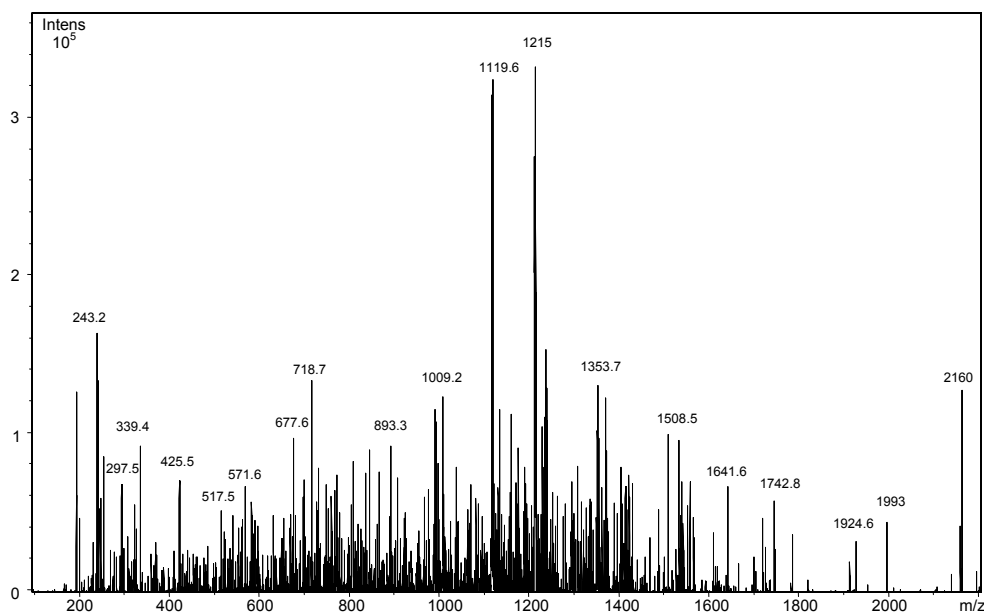


Fig. 5 – MS spectrum of polysiloxane modified with timine.

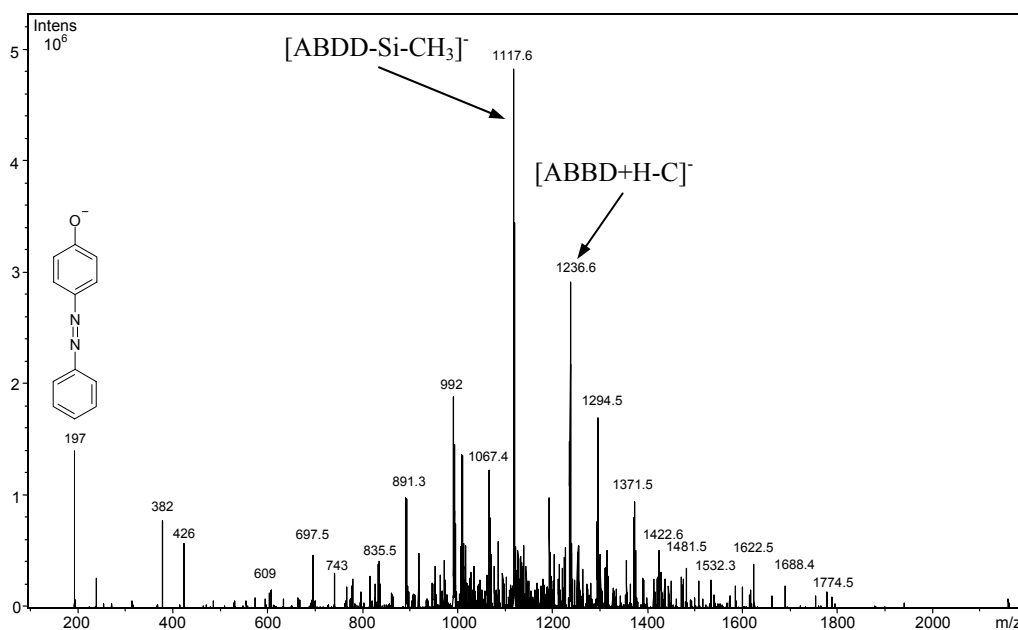


Fig. 6 – MS spectrum of polysiloxane modified with azobenzene and citozine.

Some of the spectral lines seem to be combinations of fragment mass of the three units taking part to the polymeric chains. Their combinations using the groups identified above are given in Fig. 6. The two most abundant fragments, situated at  $m/z = 1117$  and  $1236$  can be assigned to the corresponding scissions in polymeric chain, resulting in cyclic structures and followed by elimination of Si atom and a methyl group, or carbon atom plus hydrogen transposition, respectively. The fragment corresponding to

azobenzene elimination from side groups is present in experimental spectrum, as previously mentioned.

The APCI-MS spectrum of polysiloxane modified with crown azo-ether 18C6 (its structure is given together with spectral interpretation) is represented in Fig. 7. From the many spectral signals the fragment  $m/z = 956$  might be assigned using the monomer mass fragment as  $660 + 74n$ . From the equality one obtains that  $n = 4$ .

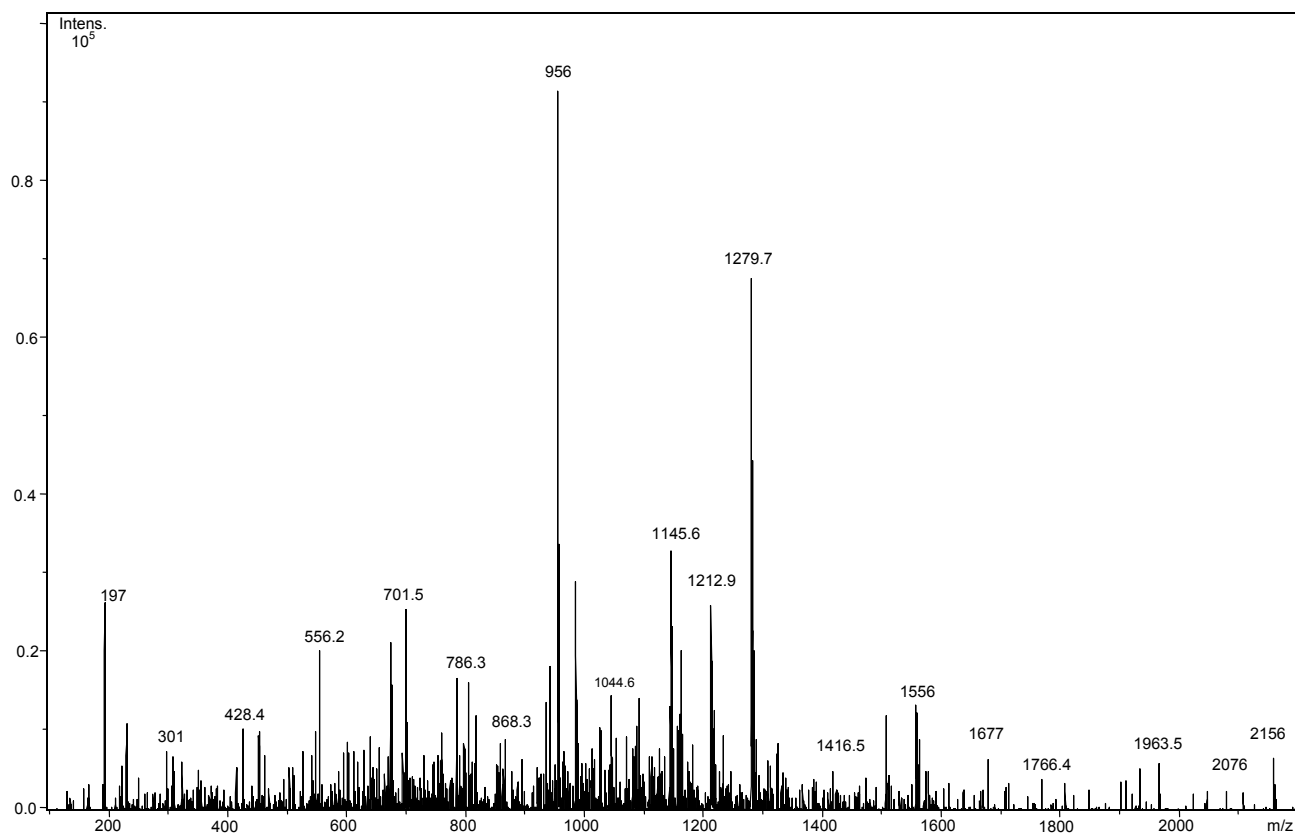


Fig. 7 – MS spectrum of polysiloxane modified with crown azo-ether 18C6.

The isolation of ion fragment with  $m/z = 704$  and its subsequent collisional induced

fragmentation leads to a MS-MS spectrum given in Fig. 8.

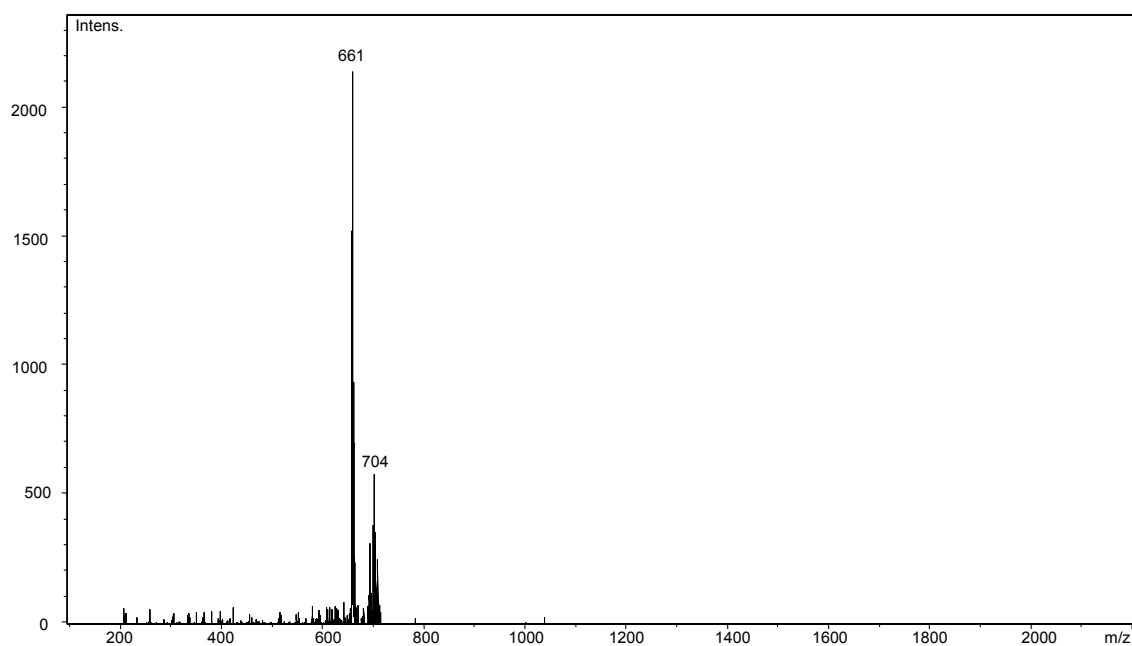
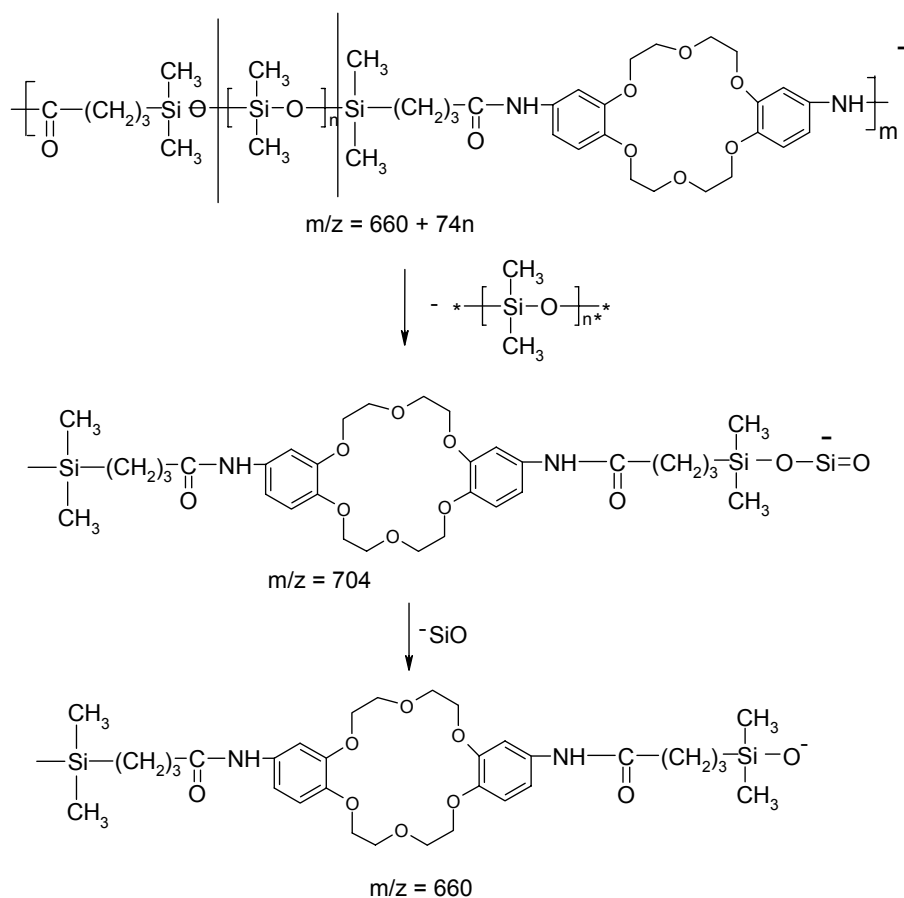


Fig. 8 – MS-MS spectrum of polysiloxane modified with crown azo-ether 18C6.

In this case, the possible fragmentation route of this polysiloxane is given in the next sequence.



The fragment situated at  $m/z = 1280$  could be a dimeric form of the previous fragment ion, with elimination of dimethylsiloxane groups from its structure. The complex structure of the siloxane polymer does not however allow a certain interpretation of the experimental spectral line.

by lack of homogeneity of the polymeric bulk used in these experiments.

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## CONCLUSIONS

The experimental mass spectra of the investigated compounds revealed that the functional group attached to the main chain of the polymer could influence the fragmentation pathway, possible through flexibility of the main chain and the stability of the functional groups under APCI conditions. Steric and polar interactions between functional groups on the same chain or on different chain may also influence the fragmentation occurring during this process. The mass spectrum can allow their identification from each other, but their patterns are not so far related to the ratio between monomeric constituents of the polymeric chains, excepting a few cases. A difficulty in this respect is possible to be explained

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