ELSEVIER

Polymer Vol. 37 No. 5, pp. 777–783, 1996

0032-3861/96/$15.00+0.00

Triazine-based polymers: 4. MALDI-MS of triazine-based polyamines*

Dietrich Braun†, Reza Ghahary and Harald Pasch
Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, 64289 Darmstadt, Germany

Due to their poor solubility in organic solvents, triazine-based polyamines are very difficult to characterize with respect to chemical structure and molar mass. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is shown to be a unique method for investigating both the reaction between substituted 2,4-dichloro-s-triazines and diamines, and the chemical structure of the reaction products. Using formic acid as the solvent and 2,5-dihydroxybenzoic acid as the matrix, well-resolved spectra are obtained and oligomer series with different end groups are identified. It is shown that partial hydrolysis of the chlorine groups of the s-triazine which leads to chain termination, may be prevented by changing the catalyst. Investigation of the reaction of a s-triazine with phenylene diamine revealed that in addition to the incorporation of phenylene diamine into the polymer chain, the self-condensation product, 2,7-diaminophenazine is incorporated as an end group. Although quantitative information on the composition of the products cannot be obtained directly at present, the qualitative description of the polycondensation process by MALDI-MS is very valuable for further investigations.

(Keywords: triazine-based polymers; chemical structure; matrix-assisted laser desorption/ionization mass spectrometry)

INTRODUCTION

Aromatic polyamides are important high-temperature-resistant polymeric materials[1]. However, their outstanding chemical stability and mechanical properties are accompanied by difficulties in manufacture and processing. The synthesis of polymers containing triazine rings instead of aromatic dicarboxylic acid units in the polymer backbone has been reported[2–5]. In particular, the reaction of 6-substituted 2,4-dichloro-s-triazines with diols results in triazine-based polyethers with interesting properties[6,7].

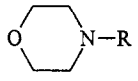
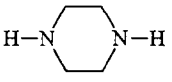
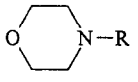
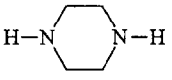
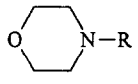
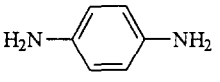
Recently, the synthesis of triazine-based polyamines from 6-substituted 2,4-dichloro-s-triazines and diamines was reported by some of the authors[8]. In brief, 16 triazine-based polyamines were prepared by interfacial polycondensation. The effect of the reaction parameters on the yield and viscosity properties was investigated. However, due to very poor solubility of the reaction products in organic solvents, chemical structure analysis proved very difficult. The reduced specific viscosity was determined in formic and trifluoroacetic acids, but size exclusion chromatography experiments could not be conducted due to a lack of suitable solvents. For the same reason a proper end group analysis could not be carried out.

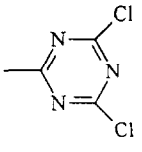
Mass spectrometry has become a viable technique for the characterization of synthetic polymers of low molar mass. The power of mass spectrometry lies in its fast and accurate determination of molar masses, the sequence of repeat units, polymer additives and impurities. The main barriers for mass spectrometry of high molar mass compounds, caused by the low volatility and thermal instability of polymers, have been overcome by the development of soft ionization techniques, such as secondary ion mass spectrometry[9,10] and field desorption[11,12]. CO_2-laser desorption combined with either a time-of-flight or a Fourier transform mass analyser, yields molecular ion peaks for a number of polymers up to 10 000 Da[13,14].

A new, most promising method for the separation of large molecules according to their molar mass and functionality has been introduced recently. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), developed by Karas and Hillenkamp in 1988[15], has been successfully used to determine the mass of large biomolecules and synthetic polymers[16,17]. The accessible mass range has been extended considerably, and the technique is fast and instrumentally very simple. Moreover, relatively inexpensive commercial instrumentation has become available. In principle, the sample to be investigated and a matrix solution are mixed in such a ratio that matrix separation of the sample molecules is achieved. After drying, a laser pulse is directed onto the solid matrix to photo-excite the matrix material. This excitation causes the matrix to explode, resulting in the expulsion and soft ionization of the sample molecules without fragmentation. Once the analyte is ionized, it is accelerated and analysed in a time-of-flight (t.o.f.) mass spectrometer. As a result, the analyte is separated according to the molar mass of its components and, in the case of heterogeneous polymers, a molar mass distribution may be obtained. In a number of papers it

* For Parts 1–3 see refs 6–8, respectively
† To whom correspondence should be addressed

Table 1 Triazine-based polyamines investigated by MALDI-MS

Sample	Triazine	Diamine	Catalyst
1			NaOH
2			$NaHCO_3$
3	C_2H_5O-R	$H_2N-(CH_2)_6-NH_2$	NaOH
4			NaOH

R: 

was shown that technical polymers may be analysed up to molar masses of about 200 000 Da[18,19]. Recently it was shown by us that epoxy resins may be separated into their oligomers according to the degree of polymerization and the type of functional groups[20]. Poly(ethylene oxide)s and poly(methyl methacrylate)s can successfully be investigated with respect to their functional end groups[21,22].

The present report describes the investigation of triazine-based polyamines by MALDI-MS. The identification of different reaction products will be discussed and it will be shown that MALDI-MS experiments provide useful information on the reaction mechanism.

EXPERIMENTAL

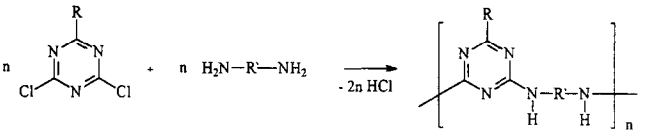
The synthesis of the triazine-based polyamines was described in detail in a previous report[8]. Further details are given in *Table 1*.

The MALDI-MS investigations were conducted on a Kratos Kompact MALDI 3. A pulsed nitrogen laser producing a wavelength of 337 nm was used for laser desorption/ionization. A t.o.f. mass spectrometer with 20 kV acceleration voltage was used to obtain mass spectra.

The samples were dissolved in formic acid at a concentration of 2–4 mg ml^{-1} and mixed with the matrix 2,5-dihydroxybenzoic acid (10 mg ml^{-1} solution in formic acid). After drying the mixture of the sample and matrix on the sample holder, the measurements were carried out using the following conditions: polarity, positive; flight path, reflection; mass, high (20 kV acceleration voltage); 100 shots per sample.

RESULTS AND DISCUSSION

The triazine-based polyamines were prepared by interfacial polycondensation of 6-substituted 2,4-dichloro-s-triazines with various diamines according to the following general reaction scheme:



Scheme 1

The triazines were dissolved in chloroform, toluene or nitrobenzene, whereas the diamines were dissolved in water. A base was added to the aqueous phase for deactivation of the hydrochloric acid formed during the polycondensation.

Depending on the reactant ratios and the reaction conditions, oligomers having different end groups may be formed. With an excess of the dichlorotriazine in the reaction mixture, predominantly triazine end groups are assumed to be formed. Vice versa, an excess of the diamine should lead predominantly to amine end groups. With an equimolar ratio of the reactants, oligomers with mixed end groups are likely to be formed. Due to the poor solubility of the reaction products, an end group analysis via titration could not be conducted.

The MALDI-MS spectrum of a typical reaction product (sample 1) is shown in *Figure 1*. Each peak in the spectrum represents one oligomer with a certain mass, characterizing the degree of polymerization (n) and the type of end groups of this specific oligomer. The peaks can be assigned to a number of peak series having equal peak-to-peak mass increments of 249 Da. This mass increment exactly equals the mass of the repeating unit in the polyamines. Accordingly, all peaks indicated with the same number belong to one homologous series.

At least five different homologous series are obtained in the spectrum, see numbers 1–5 in the inset of Figure 1. For example, the peaks at 1531 Da, 1779 Da, 2027 Da and so on belong to homologous series 1, whereas the peaks at 2327 Da, 2576 Da, 2825 Da and so on belong to series 2. They are due to intact oligomers cationized by the attachment of H^+ from the matrix to form $M + H^+$ molecular ions.

The appearance of different homologous series having the same polymer backbone is obviously the result of the formation of different end groups. From the total masses of the oligomers and the mass of the polymer backbone, the masses of the end groups may be calculated and assigned to a certain chemical structure. For example, taking the peak at $M + H^+ = 1779$ Da and subtracting the mass of the repeating unit several times, one ends up with a mass of 35 Da for the end groups, assuming that the degree of polymerization $n = 7$:

$$M + H^+ = 1779\,\text{Da} = 36 + 249n$$

$$M = 1778\,\text{Da} = 35 + 249n$$

end group — polymer backbone

An end group mass of 35 Da can be assigned to an oligomer with the following chemical structure (accuracy

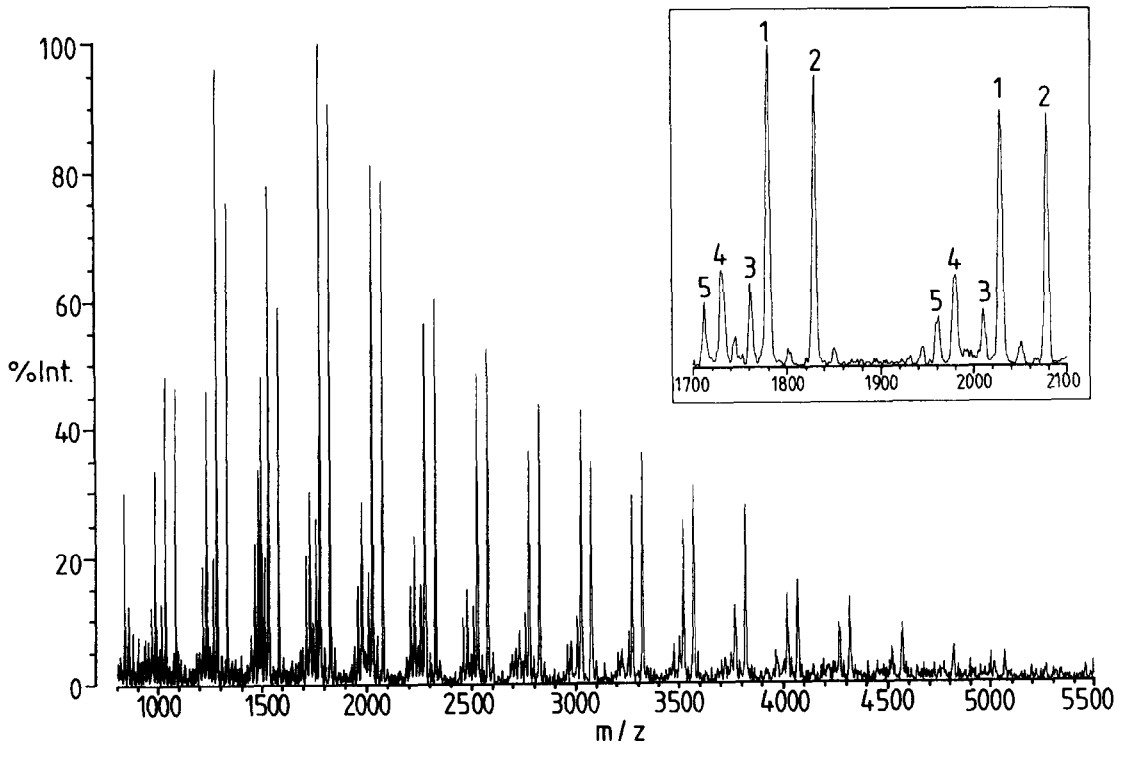


Figure 1 MALDI-MS spectrum of sample 1 (numbers indicate homologous series)

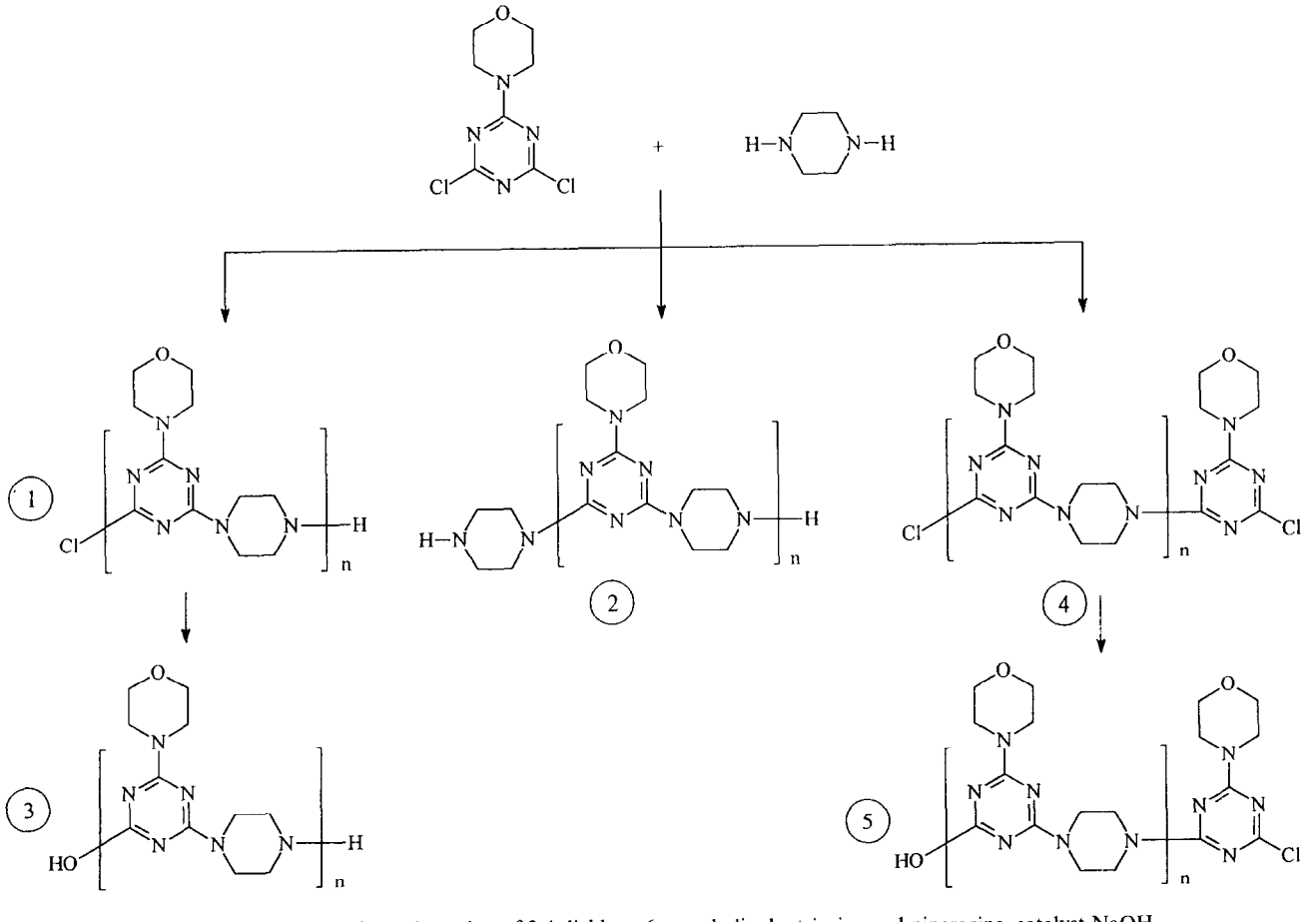


Figure 2 Reaction mechanism of the polycondensation of 2,4-dichloro-6-morpholinyl-s-triazine and piperazine, catalyst NaOH

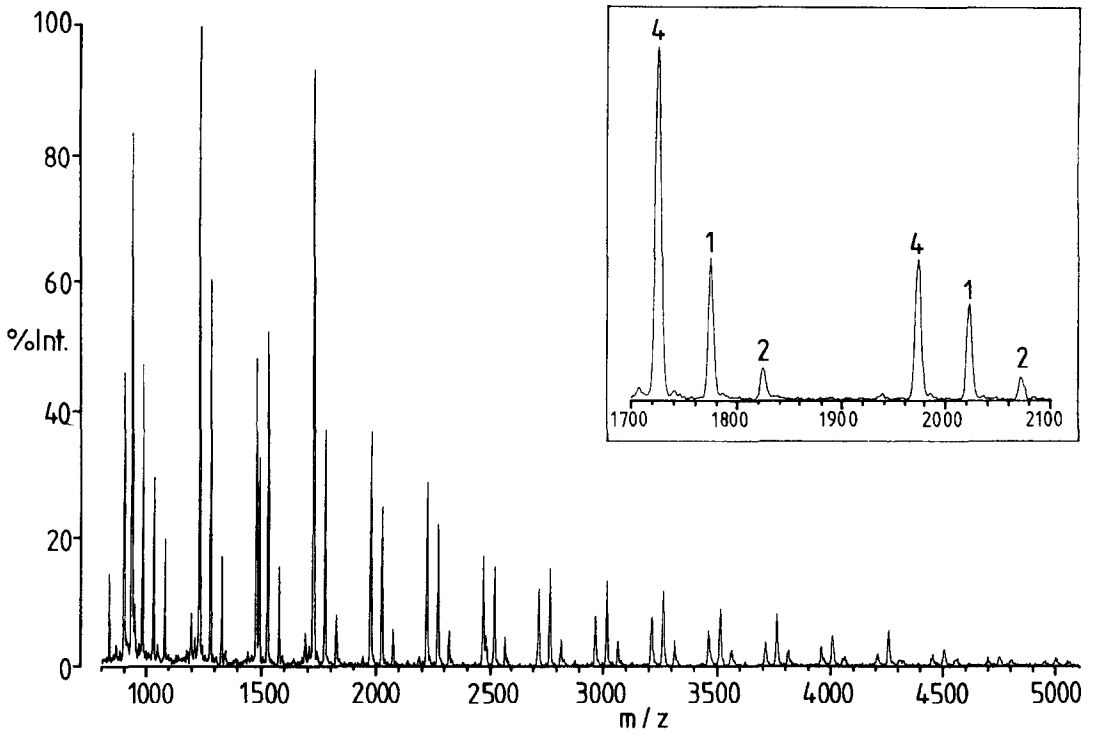


Figure 3 MALDI-MS spectrum of sample 2 (numbers indicate homologous series)

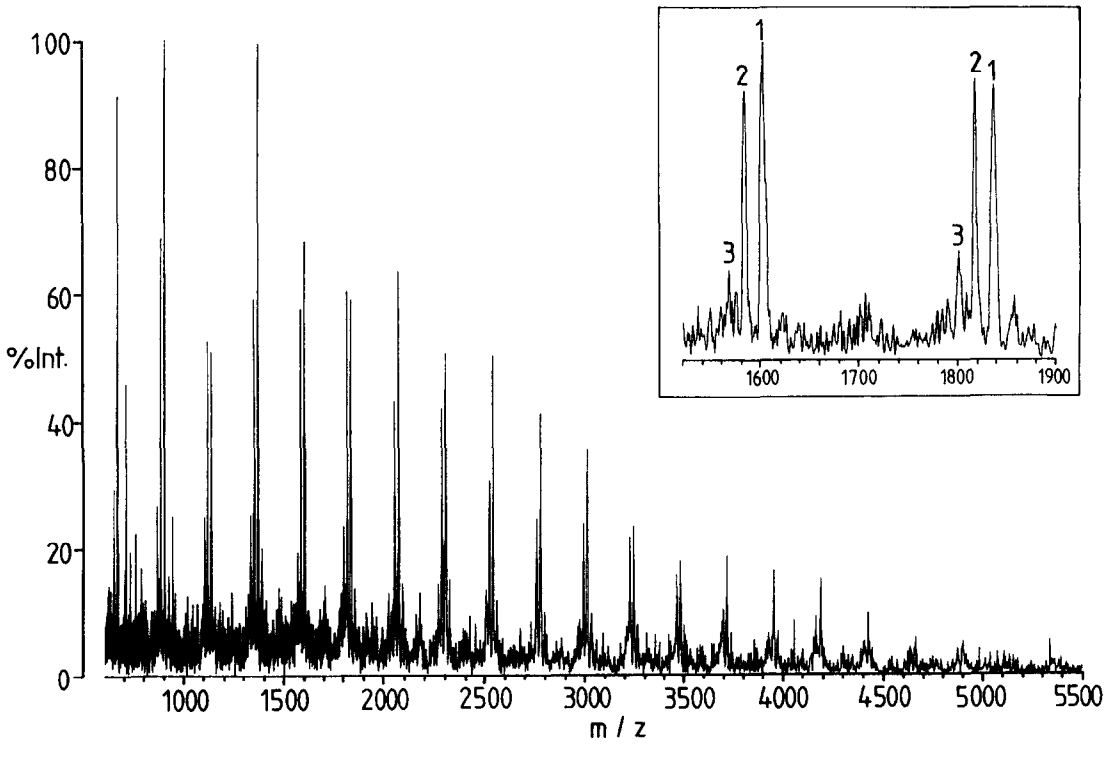
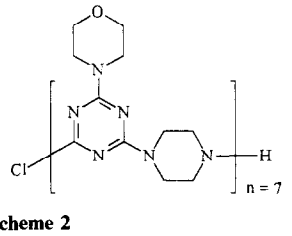


Figure 4 MALDI-MS spectrum of sample 3 (numbers indicate homologous series)

of mass determination is ±1 Da):



M (determined) = 1778 g mol^{-1}
M (calculated) = 1779 g mol^{-1}

Scheme 2

In a similar way all other homologous series may be analysed, giving the masses of the end groups and their chemical structure, accordingly;

(1) $M = 35 + 249n$
(2) $M = 87 + 249n$
(3) $M = 17 + 249n$
(4) $M = 237 + 249n$
(5) $M = 217 + 249n$

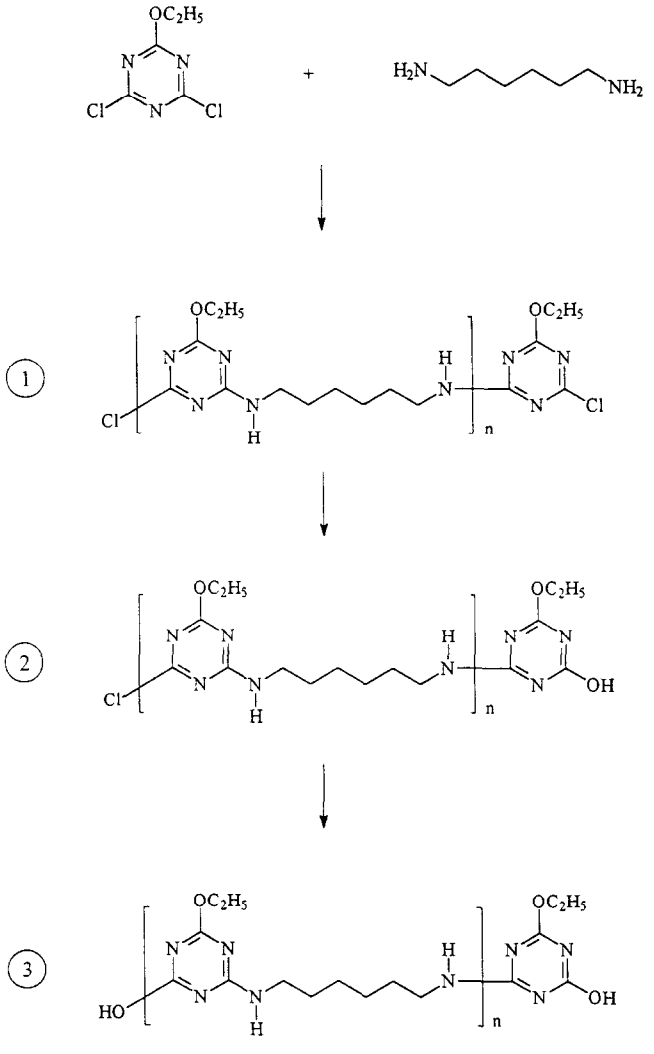


Figure 5 Reaction mechanism of the polycondensation of 2,4-dichloro-6-ethoxy-s-triazine and 1,6-hexamethylene diamine

In agreement with our expectations, homologous series with an amino and a chlorotriazine end group (series 1) and two amino end groups (series 2) can be identified as the main fractions. In addition, a third fraction with two chlorotriazine end groups (series 4) is present in the reaction product. The homologous series 3 and 5 are assumed to be formed by partial hydrolysis of the chlorine at the triazine end group to a hydroxy function. The proposed reaction mechanism is summarized in *Figure 2*.

The hydrolysis of the chlorotriazine end groups is a side reaction which leads to end group deactivation, and subsequent chain termination. This reaction is obviously accelerated by the aqueous NaOH present in the reaction mixture. Assuming that a weaker base would reduce hydrolysis, $NaHCO_3$ was used instead of NaOH. The MALDI-MS spectrum of the reaction product, shown in *Figure 3*, clearly confirms this assumption. Peak series 3 and 5, which belong to the hydrolysis products are not present in the spectrum.

In another experiment, 6-ethoxy-2,4-dichloro-s-triazine was reacted with hexamethylene diamine (sample 3). In this case the MALDI-MS spectrum indicates that only oligomers with triazine end groups are formed, see *Figure 4*. Similar to the previous results, species with hydroxy-triazine end groups are formed to a significant extent, indicating that partial hydrolysis has to be accounted for, see reaction scheme in *Figure 5*.

The reaction of 2,4-dichloro-6-morpholinyl-s-triazine with *p*-phenylene diamine (sample 4) leads to a coloured product, which even after extensive purification procedures keeps its colour. Therefore, it must be assumed that the colour is not due to any impurity in the reaction mixture but due to the incorporation of a coloured moiety into the polymer chain. The MALDI-MS spectrum of sample 4 shows that, in addition to the expected homologous series 1, 2 and 3, two other

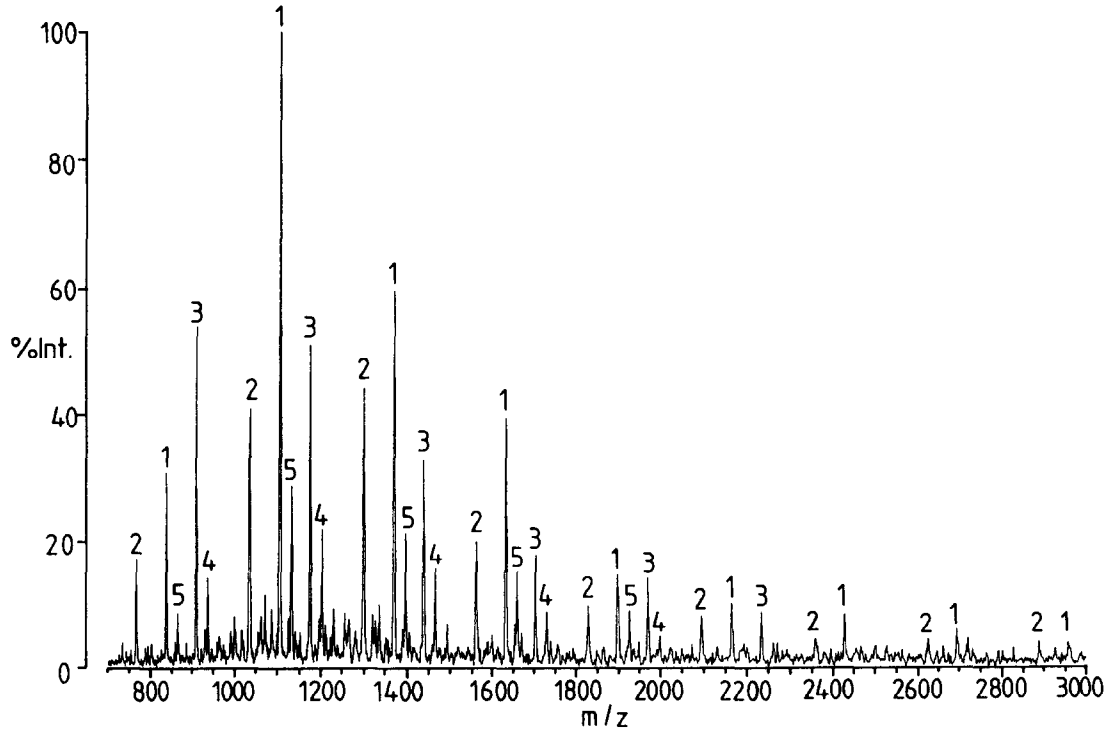


Figure 6 MALDI-MS spectrum of sample 4 (numbers indicate homologous series)

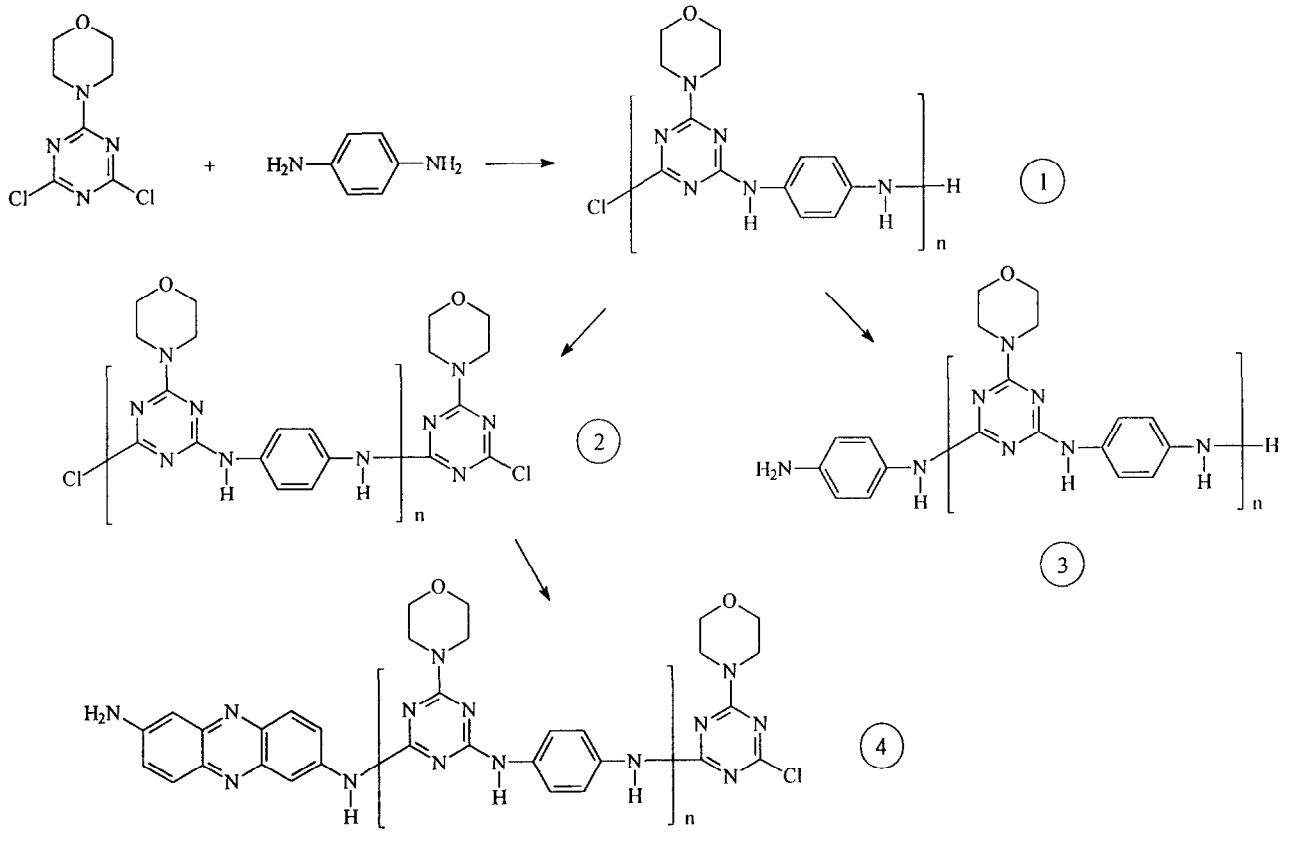
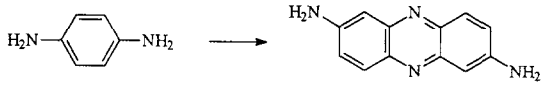


Figure 7 Reaction mechanism of the polycondensation of 2,4-dichloro-6-morpholinyl-s-triazine and phenylene diamine

homologous series (indicated with numbers 4 and 5) are obtained, see *Figure 6*.

It is known from the literature that *p*-phenylene diamine can undergo self-condensation forming coloured compounds such as 2,7-diaminophenazine[23]:



Scheme 3

This coloured diamine, of course, can also participate in the polycondensation reaction with the dichlorotriazine. Accordingly, 2,7-diaminophenazine may be incorporated into the polymer chain or at the chain end. The calculation of the mass of the end group in series 4 agrees well with this assumption, and indeed series 4 is a homologous series having a phenazine end group, see *Figure 7*. The calculation of the mass of the end group in series 5 gives 65 Da. Unfortunately we were not able to correlate this number with a chemical structure.

In conclusion, MALDI-MS is a useful technique for the characterization of triazine-based polyamines. Using MALDI-MS, it is possible to determine the chemical structure of reaction products and to identify oligomer series with different end groups. Side reactions may be identified and reaction procedures may be optimized via MALDI-MS analysis. Although quantitative information on the composition of the products cannot be obtained directly at this stage of work, the qualitative description of the polycondensation process by MALDI-MS is very valuable for further investigations.

ACKNOWLEDGEMENTS

The authors thank Degussa AG for providing some of the triazine derivatives and for supporting this investigation.

REFERENCES

1 Preston, J. *Angew. Makromol. Chem.* 1982, **109/110**, 1
2 Audebert, R. and Neel J. *Bull. Soc. Chim. France* 1970, 606
3 Kutepov, D. F. and Kogan, N. N. *Vysokomol. Soedin., Ser. B* 1970, **12**, 344
4 Wang, D. W. and Fischer, M. M. *J. Polym. Sci., Polym. Chem.* 1983, **21**, 671
5 Mikroyannidis, J. A. *J. Polym. Sci., Polym. Chem.* 1988, **26**, 583
6 Braun, D. and Ziser, T. *Angew. Makromol. Chem.* 1994, **219**, 27
7 Braun, D. and Ziser, T. *Angew. Makromol. Chem.* 1994, **221**, 187
8 Braun, D., Ghahary, R. and Ziser, T. *Angew. Makromol. Chem.* 1995, **233**, 121
9 Leyen, D. V., Hagenhoff, B., Niehuis, E., Benninghoven, A., Bletsos, I. V. and Hercules, D. M. *J. Vac. Sci. Technol.* 1989, **A7**, 1790
10 Feld, H., Leute, A., Zurmühlen, R. and Benninghoven, A. *Anal. Chem.* 1991, **63**, 903
11 Lattimer, R. P. and Schulten, H. R. *Int. J. Mass Spectrom. Ion Phys.* 1985, **67**, 227
12 Lattimer, R. P. *Int. J. Mass Spectrom. Ion Processes* 1983, **55**, 221
13 Ijames, C. F. and Wilkins, C. L. *J. Am. Chem. Soc.* 1988, **110**, 2687
14 Cotter, R. J., Honovich, J. P., Olthoff, J. K. and Lattimer, R. P., *Macromolecules* 1986, **19**, 2996
15 Karas, M. and Hillenkamp, F. *Anal. Chem.* 1988, **60**, 2299
16 Beavis, R. C. and Chait, B. T. *Rapid Commun. Mass Spectrom.* 1989, **3**, 233

17 Hillenkamp, F., Karas, M., Beavis, R. C. and Chait, B. T. *Anal. Chem.* 1991, **63**, 1193A
18 Bahr, U., Deppe, A., Karas, M., Hillenkamp, F. and Giessman, U. *Anal. Chem.* 1992, **64**, 2866
19 Danis, P. O., Karr, D. E., Mayer, F., Holle, A. and Watson, C. H. *Org. Mass Spectrom.* 1992, **27**, 843
20 Pasch, H. and Unvericht, R. *Angew. Makromol. Chem.* 1993, **212**, 191
21 Pasch, H. and Zammert, I. *Int. J. Polym. Anal. Char.* 1995, **1**, 329
22 Pasch, H. and Gores, F. *Polymer* 1995, **36**, 1999
23 'Ullmanns Enzyklopädie der technischen Chemie, 4. Auflage', Verlag Chemie, Weinheim, 1976, Vol. 13, p. 233