Study of synthetic aliphatic copolyamides by time-of-flight matrix assisted laser desorption/ionization mass spectrometry

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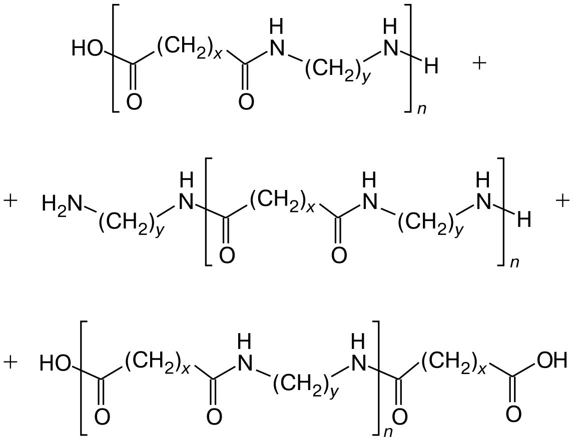
Synthetic copolyamides based on aliphatic diamines (1,3-propanediamine and 1,4-butanediamine) and dichlorides of aliphatic carboxylic acids (adipic and sebacic acid dichlorides) were investigated using time-of-flight matrix assisted laser desorption/ionization mass spectrometry. Their mass spectra showed peaks for cationized (Na^+ and K^+) and protonated (less intense peaks) oligomers with NH_2—NH_2, NH_2—COOH, or COOH—COOH end groups. No cyclic oligomers were detected in the samples. The compositions of oligomers were determined, and the relative reactivities of homologous comonomers in polycondensation were estimated.

Key words: copolyamides, oligomers, time-of-flight mass spectrometry, matrix assisted laser desorption/ionization.

Despite the substantial progress achieved in studies of diverse synthetic polymers by matrix assisted laser desorption/ionization (MALDI) mass spectrometry, only few publications are devoted to synthetic polyamides, most of these being concerned with industrial polymers. In particular, MALDI mass spectrometry has been used to determine the molecular mass distribution of nylon-6 and products of its cleavage with amines or acids,[1] to establish the nature of the end groups in nylon-6,[2] and to study thermal *trans*-reactions in a mixture of nylon-6,6 with nylon-6,10.[3,4] Of particular interest, however, is to elucidate the scope of this method for investigation of copolyamides, both synthetic and those formed upon *trans*-reactions of homopolyamides.

In this study, the time-of-flight mass spectrometry with a soft MALDI ionization method is used to investigate some characteristics of copolyamides **1—4** (cationization type, the nature of the end groups, and, first of all, composition) synthesized deliberately on the basis of aliphatic diamines (1,3-propanediamine and 1,4-butanediamine) and aliphatic diacyl chlorides (adipoyl and sebacoyl dichlorides). The applicability of the MALDI method to evaluation of the comparative reactivity of homologous bifunctional compounds in polycondensation was studied.

For comparison, the corresponding homopolyamides were synthesized and analyzed.



1—4

1: $x = 4$; $y = 3, 4$; **2:** $x = 8$; $y = 3, 4$
3: $x = 4, 8$; $y = 3$; **4:** $x = 4, 8$; $y = 4$

This work is the first stage of research aimed at the development of a mass spectrometric technique for determination of a monomer-unit sequence in copolyamides.

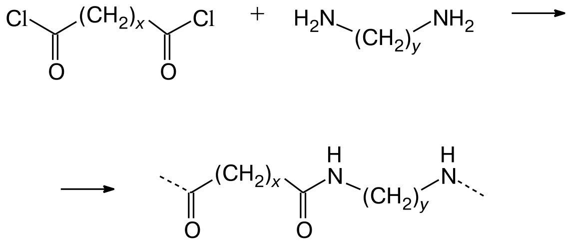
Experimental

Copolyamides **1** and **2** were prepared by stirring of equimolar amounts of diamines (1,3-propanediamine and 1,4-butane-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1320—1324, July, 2007.

diamine) with a stoichiometric amount of adipoyl and sebacoyl dichloride, respectively (Scheme 1), in the presence of pyridine without a solvent at 20 °C. Copolyamides **3** and **4** were synthesized in a similar way but using an equimolar amount of adipic and sebacic acid dichlorides and a twofold excess of 1,3-propanediamine or 1,4-butanediamine, respectively. Homopolymers were obtained by stirring equimolar amounts of appropriate acid chlorides and diamines in the presence of pyridine at 20 °C. Polycondensation was carried out without preliminary dehydration of reactants; therefore, chain termination was induced by water traces or by contact with air.

Scheme 1



The viscosity of the synthesized copolyamides **1—4** measured in formic acid as the solvent was 0.11—0.12 dL g^{-1}. This attests to the oligomeric character and relatively low average molecular weights of compounds.

The samples for analysis were prepared as follows: a 0.1 *M* solution of the matrix in THF was applied on a target, the solvent was allowed to be completely evaporated, and a polymer solution in trifluoroacetic acid (2 mg mL^{-1}) was applied onto the matrix spot and dried. The final matrix : polymer weight ratio on the target was 50 : 1 to 100 : 1. No additional dopants were used for cationization of polymers

MALDI mass spectra were measured on a Bruker Autoflex II reflectron time-of-flight mass spectrometer equipped with a nitrogen laser (λ = 337 nm). 2-(4-Hydroxyphenylazo)benzoic acid (HABA) was chosen as the matrix for recording the MALDI mass spectra, as it ensured the highest signal intensity for lower laser power among other matrices tested (*e.g.*, 2,5-dihydroxybenzoic acid, 3β-indoleacrylic acid).

Results and Discussion

The copolyamides represented two pairs of compounds prepared from two different diamines and one dichloride of dicarboxylic acid (**1**, **2**), or from one diamine and two different dichlorides (**3**, **4**). The reactants were used without preliminary removal of moisture, water molecules being actually involved in chain termination. As a consequence, the resulting copolyamides had moderate molecular weights with an upper boundary of only 3000 Da. In view of the evidently high polydispersity of the copolyamides and the presence of low-molecular-weight oligomers, we did not determine the molecular-weight distribution of the samples.

It is known that[5] during matrix assisted laser desorption/ionization, macromolecules add metal cations (most often, Na^+ and K^+ ions present in trace amounts in solvents or coming from the vessel walls) or protons; the ions thus formed possess relatively low energy usually insufficient for the subsequent fragmentation. As shown by analysis of the MALDI mass spectra of polymers **1—4**, ionization in this case is also associated with the attachment of Na^+ (to a higher extent) or K^+ ions to oligomeric molecules, whereas protonated molecules form to a minor extent. The diversity of the cationic forms of oligomers, the presence of different end groups in macromolecules, and a broad scatter of molecular weights account for the complex mass spectral patterns (Figs 1 and 2).

Since all of the peaks present in the copolyamide mass spectra are due to only cationized oligomers, which are not destroyed to form fragment ions, their mass numbers and intensities can be used to calculate the molecular-weight characteristics and to determine structural elements. The mass spectroscopic data were processed using a specially written simple computer program, which allows one to relate the mass number of ions (m/z) to the monomer composition of the oligomers, the type of end groups, and the nature of the attached cations:

$$m/z = (\mathrm{DAm})^1{}_n(\mathrm{DAm})^2{}_l(\mathrm{DAc})_m + E_1 + E_2 + \mathrm{Cat}^+$$

(for co-polyamides formed by two different diamines and one dicarboxylic acid),

$$m/z = (\mathrm{DAm})_n(\mathrm{DAc})^1{}_l(\mathrm{DAc})^2{}_m + E_1 + E_2 + \mathrm{Cat}^+$$

(for co-polyamides formed by one diamine and two different acids), where DAm and DAc are the masses of the amine and acid residues, respectively, *n*, *l*, and *m* are the numbers of these residues in the oligomer molecule, E_1 and E_2 are the masses of the H atom (for the terminal amino group) or the OH group (for the terminal carboxylic group), Cat^+ is the cation mass.

Using this program, it is possible to determine the oligomer composition and the nature of end groups (the key results of processing of the MALDI mass spectra of polymers **2** and **4** are presented in Tables 1 and 2).* In this particular case, the use of the program was easier due to the fact that only Na^+, K^+, and H^+ were the cations likely to add. Indeed, closely spaced groups of peaks always contained ion peaks with mass differing by 16 units, which corresponds to the difference between sodium (23) and potassium (39). The masses of protonated molecules are 22 and 38 Da lower that those of Na^+- and K^+- containing products, respectively. Of equal importance for calculations was the assumption that only carboxy or amino groups in various combinations may be present as the end groups.

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* For short, the composition of polymers is expressed by single letters designating the fragments of 1,3-propanediamine (**P**), 1,4-butanediamine (**B**), adipic acid (**A**), and sebacic acid (**S**).

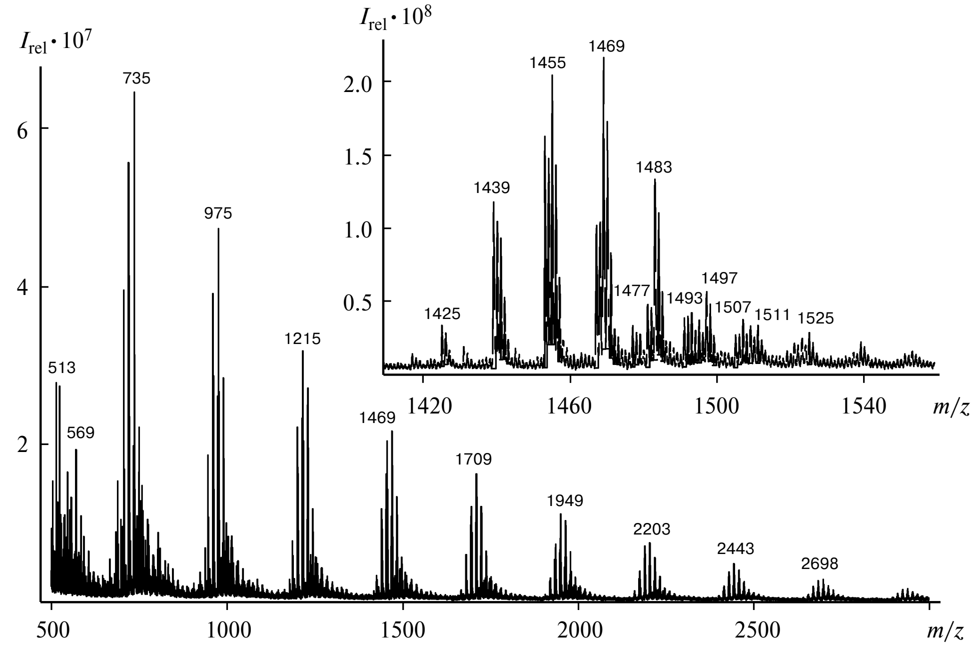

Fig. 1. MALDI TOF mass spectrum of polymer **2** (the assignment of ion peaks for the enlarged region is given in Table 1).

Table 1. Composition of ions for the enlarged region of the spectrum of polymer **2** (see Fig. 1)

m/z	I_{rel} (%)	Composition of the ion	End groups
1417	2	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_1 + \mathrm{H}$	COOH—COOH
1425	5	$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_0 + \mathrm{Na}$	COOH—COOH
1431	3	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_2 + \mathrm{H}$	COOH—COOH
1439	18	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_1 + \mathrm{Na}$	COOH—COOH
1441	14	$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_0 + \mathrm{K}$	COOH—COOH
1445	3	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_3 + \mathrm{H}$	COOH—COOH
1453	25	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_2 + \mathrm{Na}$	COOH—COOH
1455	32	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_1 + \mathrm{K}$	COOH—COOH
1459	3	$\mathbf{S}_6\mathbf{P}_6\mathbf{B}_0 + \mathrm{H}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_1\mathbf{B}_4 + \mathrm{H}$	COOH—COOH
1467	17	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_3 + \mathrm{Na}$	COOH—COOH
1469	34	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_2 + \mathrm{K}$	COOH—COOH
1473	4	$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_1 + \mathrm{H}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_0\mathbf{B}_5 + \mathrm{H}$	COOH—COOH
1481	8	$\mathbf{S}_6\mathbf{P}_6\mathbf{B}_0 + \mathrm{Na}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_1\mathbf{B}_4 + \mathrm{Na}$	COOH—COOH
1483	21	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_3 + \mathrm{K}$	COOH—COOH
1487	4	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_2 + \mathrm{H}$	NH_2—COOH
1495	6	$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_1 + \mathrm{Na}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_0\mathbf{B}_5 + \mathrm{Na}$	COOH—COOH
1497	9	$\mathbf{S}_6\mathbf{P}_6\mathbf{B}_0 + \mathrm{K}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_1\mathbf{B}_4 + \mathrm{K}$	COOH—COOH
1501	2	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_3 + \mathrm{H}$	NH_2—COOH
1509	5	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_2 + \mathrm{Na}$	NH_2—COOH
1511	5	$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_1 + \mathrm{K}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_0\mathbf{B}_5 + \mathrm{K}$	COOH—COOH
1515	2	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_4 + \mathrm{H}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_7\mathbf{B}_0 + \mathrm{H}$	NH_2—NH_2
1523	4	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_3 + \mathrm{Na}$	NH_2—COOH
1525	4	$\mathbf{S}_6\mathbf{P}_4\mathbf{B}_2 + \mathrm{K}$	NH_2—COOH
1529	2	$\mathbf{S}_6\mathbf{P}_1\mathbf{B}_5 + \mathrm{H}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_6\mathbf{B}_1 + \mathrm{H}$	NH_2—NH_2
1537	2	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_4 + \mathrm{Na}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_7\mathbf{B}_0 + \mathrm{Na}$	NH_2—NH_2
1539	3	$\mathbf{S}_6\mathbf{P}_3\mathbf{B}_3 + \mathrm{K}$	NH_2—COOH
1543	2	$\mathbf{S}_6\mathbf{P}_0\mathbf{B}_6 + \mathrm{H}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_5\mathbf{B}_2 + \mathrm{H}$	NH_2—NH_2
1551	2	$\mathbf{S}_6\mathbf{P}_1\mathbf{B}_5 + \mathrm{Na}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_6\mathbf{B}_1 + \mathrm{Na}$	NH_2—NH_2
1553	3	$\mathbf{S}_6\mathbf{P}_2\mathbf{B}_4 + \mathrm{K}$	NH_2—COOH
		$\mathbf{S}_6\mathbf{P}_7\mathbf{B}_0 + \mathrm{K}$	NH_2—NH_2

The calculations have shown that one *m/z* value may correspond to two or more oligomer compositions, end groups, and cations (isobaric ions) (see Tables 1 and 2). However, for most peaks without superimposition of isobaric ions, the monomeric composition of the oligomer could be determined unambiguously. On the basis of computation, it was shown that in all cases, the mixture consisted of oligomers with three types of end groups, NH_2—NH_2, NH_2—COOH, and COOH—COOH (their structures are given above). No cyclic oligomers were detected. The presence of peaks with equal mass numbers in the mass spectra of copolyamides and homopolyamides confirms that the latter are formed during copolymerization; this also follows from computation results.

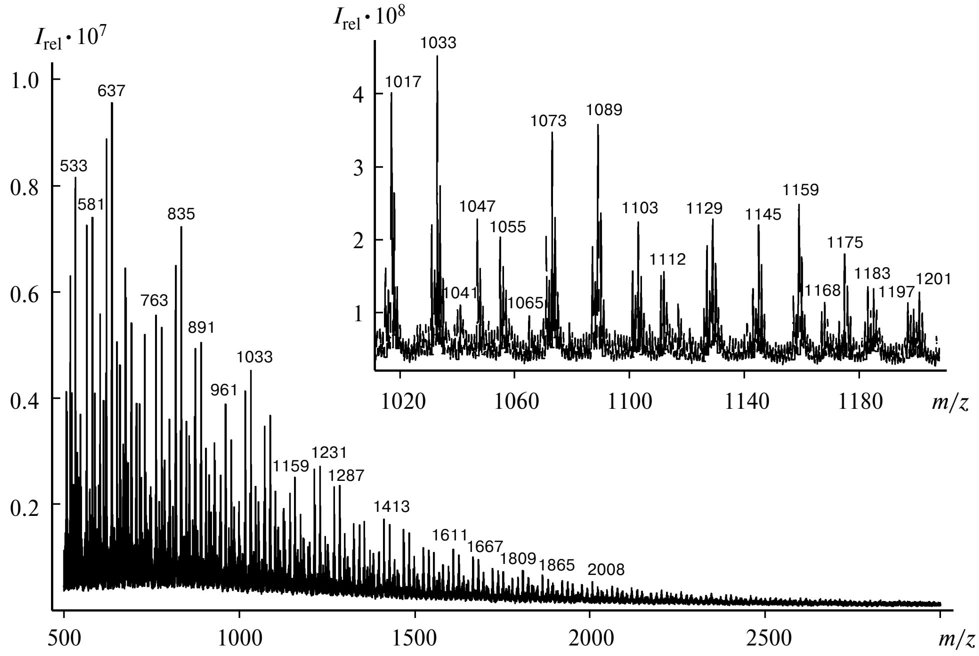

Fig. 2. MALDI TOF mass spectrum of polymer **4** (the assignment of ion peaks for the enlarged region is given in Table 2).

Table 2. Composition of ions for the enlarged region of the spectrum of polymer **4** (see Fig. 2)

m/z	I_{rel} (%)	Composition of the ion	End groups
1017	43	$\mathbf{B}_4\mathbf{A}_1\mathbf{S}_3$ + K	NH_2—COOH
		$\mathbf{B}_4\mathbf{A}_4\mathbf{S}_1$ + Na	COOH—COOH
1031	23	$\mathbf{B}_5\mathbf{A}_5\mathbf{S}_0$ + Na	NH_2—COOH
		$\mathbf{B}_5\mathbf{A}_2\mathbf{S}_2$ + K	NH_2—NH_2
1033	47	$\mathbf{B}_4\mathbf{A}_4\mathbf{S}_1$ + K	COOH—COOH
1035	15	$\mathbf{B}_4\mathbf{A}_0\mathbf{S}_4$ + H	NH_2—COOH
1047	24	$\mathbf{B}_5\mathbf{A}_5\mathbf{S}_0$ + K	NH_2—COOH
1049	11	$\mathbf{B}_5\mathbf{A}_1\mathbf{S}_3$ + H	NH_2—NH_2
1051	9	$\mathbf{B}_4\mathbf{A}_3\mathbf{S}_2$ + H	COOH—COOH
1057	14	$\mathbf{B}_4\mathbf{A}_0\mathbf{S}_4$ + Na	NH_2—COOH
1065	10	$\mathbf{B}_5\mathbf{A}_4\mathbf{S}_1$ + H	NH_2—COOH
1071	21	$\mathbf{B}_5\mathbf{A}_1\mathbf{S}_3$ + Na	NH_2—NH_2
1073	36	$\mathbf{B}_4\mathbf{A}_0\mathbf{S}_4$ + K	NH_2—COOH
		$\mathbf{B}_4\mathbf{A}_3\mathbf{S}_2$ + Na	COOH—COOH
1079	9	$\mathbf{B}_6\mathbf{A}_5\mathbf{S}_0$ + H	NH_2—NH
1087	20	$\mathbf{B}_5\mathbf{A}_4\mathbf{S}_1$ + Na	NH_2—COOH
		$\mathbf{B}_5\mathbf{A}_1\mathbf{S}_3$ + K	NH_2—NH_2
1089	38	$\mathbf{B}_4\mathbf{A}_3\mathbf{S}_2$ + K	COOH—COOH
1101	16	$\mathbf{B}_6\mathbf{A}_5\mathbf{S}_0$ + Na	NH_2—NH_2
1103	24	$\mathbf{B}_5\mathbf{A}_4\mathbf{S}_1$ + K	NH_2—COOH
1105	10	$\mathbf{B}_5\mathbf{A}_0\mathbf{S}_4$ + H	NH_2—NH_2
1107	9	$\mathbf{B}_4\mathbf{A}_2\mathbf{S}_3$ + H	COOH—COOH
1117	12	$\mathbf{B}_6\mathbf{A}_5\mathbf{S}_0$ + K	NH_2—NH_2
1121	8	$\mathbf{B}_5\mathbf{A}_3\mathbf{S}_2$ + H	NH_2—COOH
1127	20	$\mathbf{B}_5\mathbf{A}_0\mathbf{S}_4$ + Na	NH_2—NH_2
1129	24	$\mathbf{B}_4\mathbf{A}_2\mathbf{S}_3$ + Na	COOH—COOH
1135	7	$\mathbf{B}_6\mathbf{A}_4\mathbf{S}_1$ + H	NH_2—NH_2
1137	7	$\mathbf{B}_5\mathbf{A}_6\mathbf{S}_0$ + H	COOH—COOH
1143	14	$\mathbf{B}_5\mathbf{A}_3\mathbf{S}_2$ + Na	NH_2—COOH
		$\mathbf{B}_5\mathbf{A}_0\mathbf{S}_4$ + K	NH_2—NH_2
1145	23	$\mathbf{B}_4\mathbf{A}_2\mathbf{S}_3$ + K	COOH—COOH
1157	13	$\mathbf{B}_6\mathbf{A}_4\mathbf{S}_1$ + Na	NH_2—NH_2
1159	26	$\mathbf{B}_5\mathbf{A}_3\mathbf{S}_2$ + K	NH_2—COOH
		$\mathbf{B}_5\mathbf{A}_6\mathbf{S}_0$ + Na	COOH—COOH
1163	7	$\mathbf{B}_4\mathbf{A}_1\mathbf{S}_4$ + H	COOH—COOH
1173	9	$\mathbf{B}_6\mathbf{A}_4\mathbf{S}_1$ + K	NH_2—NH_2
1175	19	$\mathbf{B}_5\mathbf{A}_6\mathbf{S}_0$ + K	COOH—$COOH_2$
1177	10	$\mathbf{B}_5\mathbf{A}_2\mathbf{S}_3$ + H	NH_2—COOH
1185	14	$\mathbf{B}_4\mathbf{A}_1\mathbf{S}_4$ + Na	COOH—COOH
1191	6	$\mathbf{B}_6\mathbf{A}_3\mathbf{S}_2$ + H	NH_2—NH_2
1193	6	$\mathbf{B}_5\mathbf{A}_5\mathbf{S}_1$ + H	COOH—COOH
1199	11	$\mathbf{B}_5\mathbf{A}_2\mathbf{S}_3$ + Na	NH_2—COOH
1201	13	$\mathbf{B}_4\mathbf{A}_1\mathbf{S}_4$ + K	COOH—COOH

The results (see Tables 1 and 2) attest that the compositions of oligomeric copolyamides can often be reliably analyzed using MALDI spectra; this will be used subsequently to develop a method for determination of the lengths of unit sequences in such structures.

The plots given in Figs 3 and 4 are dependences of the intensities of sodium-cationized oligomers *vs.* composition for some copolymers with different end groups. A common trend can be followed in all cases, namely, in groups with the same number of monomer units, the peak

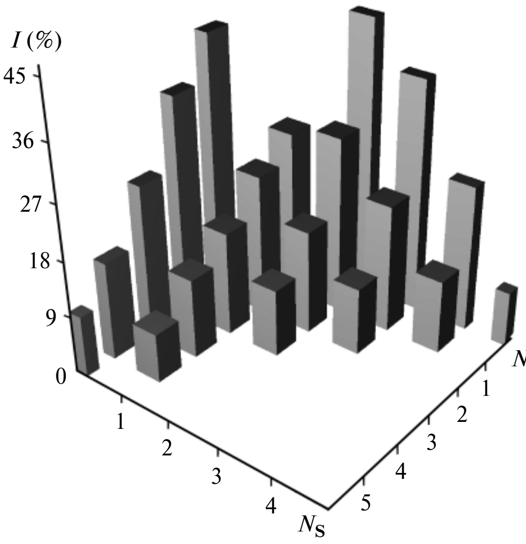

Fig. 3. Peak intensities of Na^+-cationized oligomer molecules of polymer **4** with NH_2—NH_2 end groups *vs.* composition; *N* is the number of units.

intensity decreases with an increase in the content of the heavier comonomer. Unfortunately, we have not found any data on ionization cross-sections of the homologous compounds under MALDI conditions. However, one can assume that the ionization probabilities for near homologs differ only slightly and the observed trend is indicative of a higher reactivity or mobility of the bifunctional compounds with lower mass involved in the polycondensation. These results might be helpful in investigations of kinetic parameters of co-polycondensation.

In the future, we intend to develop approaches to determination of the unit sequences in copolyamides of this type based on the results of MALDI studies.

Thus, specially synthesized aliphatic copolyamides were studied by the time-of-flight matrix assisted laser desorption/ionization mass spectrometry. The major peaks in the spectra are due to the addition products of Na^+, K^+ and (to a lesser extent) H^+ ions. The peaks were assigned by means of a dedicated computer program; this allowed identification of the end groups in particular oligomers and the monomer composition of oligomers. In the groups of peaks corresponding to ions with equal numbers of monomer units, peak intensity was found to decrease following an increase in the content of the heavier bifunctional comonomer in the oligomer. The results are indicative of good prospects for this mass spectrometry technique in determination of the structural and kinetic characteristics in the copolyamide series.

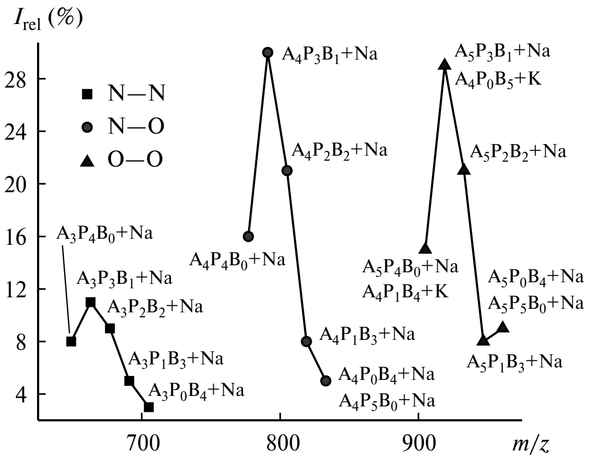

Fig. 4. Peak intensities of Na^+-cationized oligomer molecules of polymer **1** containing four dicarboxylic acid residues and having different end groups *vs.* composition.

References

1. G. Montaudo, M. S. Montaudo, C. Puglisi, and F. Samperi, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 453.
2. G. Montaudo, M. S. Montaudo, C. Puglisi, and F. Samperi, *J. Polym. Sci. A: Polym. Chem.*, 1996, **34**, 439.
3. C. Puglisi, F. Samperi, S. D. Giorgi, and G. Montaudo, *Macromolecules*, 2003, **36**, 1098.
4. F. Samperi, M. S. Montaudo, C. Puglisi, S. D. Giorgi, and G. Montaudo, *Macromolecules*, 2004, **37**, 6449.
5. H. Pasch and W. Schrepp, *MALDI-TOF Mass Spectrometry of Synthetic Polymers*, Springer, Berlin, 2003, 298 pp.

Received November 21 , 2006;
in revised form April 27, 2007