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Articles

Analysis of All-Aromatic Polyesters by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

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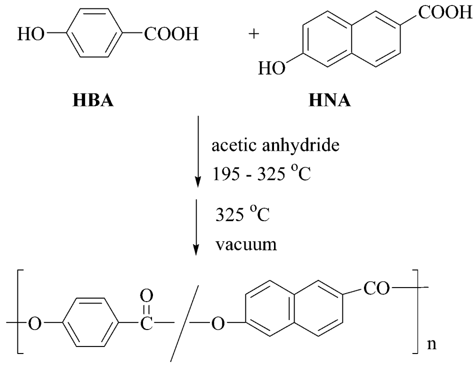
ABSTRACT: Vectra, a commercial copolymer of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), is highly intractable, and its analysis has always been problematic. Lower molecular weight polymer and an analogue have been synthesized and analyzed by MALDI−TOF mass spectrometry. Our sample preparation uses pentafluorophenol and hexafluoro-2-propanol as solvents and parafilm on the MALDI plate. In the MALDI−TOF spectra a characteristic difference was found between the copolymers synthesized using HNA with either 3-HBA or 4-HBA: the 3-HBA copolymer resulted in one main series of ions indicating no significant degradation during the polymerization, while the 4-HBA copolymer showed evidence of several depolymerization via a quinomethide mechanism. The MALDI−TOF spectra demonstrated that the distribution of the oxybenzoyl (B) and oxynaphthoyl (N) monomer units was close to the stoichiometric ratio, indicating that the reactivities of these units are very similar.

Introduction

Over the past 15 years we have conducted fundamental research on the chemistry of polyarylates and liquid crystal aromatic polyesters. Vectra is a copolymer of *p*-hydroxybenzoic acid, 4-HBA, and 6-hydroxy-2-naphthoic acid, HNA, which is currently used as a high tech engineering plastic in a variety of applications, such as electrical/electronic and health care applications. The polymerization is conducted by heating a mixture of HBA and HNA in the presence of acetic anhydride. The phenolic hydroxy end groups are converted to acetoxy groups, which react with the carboxylic acid end groups with evolution of acetic acid to form the ester linkages. We have extensively studied this seemingly simple process shown in Scheme 1.[1−3]

Scheme 1. Synthesis of Vectra



The mechanism has complications inasmuch as we found early evolution of carbon dioxide and concomitant formation of phenol. Under the polymerization conditions one may expect cleavage of the acetate end groups to ketene and the free phenolic group. The other side reaction is decarboxylation at the oxybenzoic acid ends, resulting in phenyl ester end groups. The result of these competing reactions is that the end groups change, and therefore the reaction changes mechanism during the polymerization (Scheme 2). From being an acidolysis polymerization with evolution of acetic acid, it becomes a phenolysis polymerization with evolution of phenol. This is a unique case in polymer chemistry.

Numerous unsolved questions related to the degradation of the polymer end groups and the change in mechanism from acidolysis to phenolysis remain. The intractability of the polymers is a major hurdle to analyzing the polymer. The only known solvent for Vectra is pentafluorophenol, a toxic and expensive substance. This means that the normal methods of polymer characterization and identification are inoperable.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry has been successfully used for a wide variety of polymers since the appearance of the paper by Hillenkamp and co-workers.[4] Some of these studies have concentrated on the investigation of solvent effect[5] and sample deposition.[6] Nonsoluble polymers have been analyzed by using the solvent-less technique.[7] The most intractable polymers yet studied by MALDI−TOF are certain polyamides.[8,9] Polymers structurally similar to Vectra, such as poly(bisphenol A carbonate)[10] and oligomeric poly(ethylene terephthalate),[11,12] have been successfully analyzed by MALDI−TOF. Note, however, that in contrast to our polymers these aromatic carbonates contain saturated

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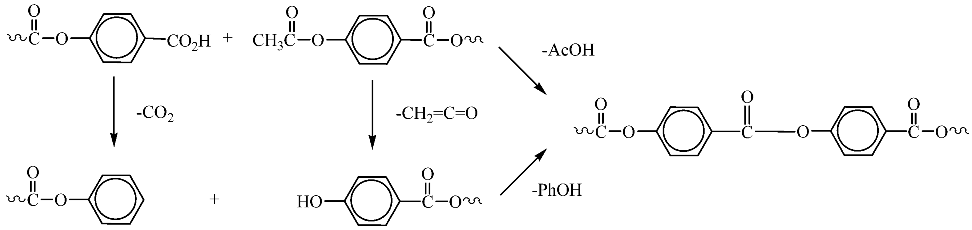
Scheme 2. Mechanism Change during Polymerization



(sp^3) carbons, and this has a strong effect on solubility. Recent reviews on the application of MALDI−TOF[13,14] and mass spectrometry in general[15] on polymer analysis provide further insight into this increasing growing and important field of research.

In the present work, we have employed MALDI−TOF to try to solve the problem of collecting information about the structure of the Vectra polymer as the reaction proceeds. Actually, it is not obvious that MALDI−TOF is capable of dealing with such an intractable polymer. To partially overcome the solubility problem and make the samples more suitable for MALDI−TOF analyses, we applied shorter polymerization reaction times (30−60 min). As expected, shorter reaction times led to lower molecular weight polymers so that the term "truncated" Vectra samples will be used throughout the paper to denote these samples.

Experimental Section

Synthesis of "Truncated Vectra" NB85 and NB86 Using 4-Hydroxybenzoic Acid. 4-Hydroxybenzoic acid, 2.00 g (14.5 mmol, 0.6 equiv), 6-hydroxy-2-naphthoic acid, 1.846 g (9.6 mmol, 0.4 equiv), and acetic anhydride, 2.706 g (26.5 mmol, 1.1 equiv), were thoroughly mixed and heated to 150 °C under reflux in argon to effect acetylation. The reflux condenser was replaced with a distillation head. The flask was heated to 250−310 °C for 30 min, and 2.7 mL (97.9%) of acetic acid was distilled. A sample was taken, chilled in liquid nitrogen, extracted twice with ether, and dried to give NB-85. Sample NB86 was synthesized similarly using a heating time of 1 h at 200−310 °C.

Synthesis of Reference Copolymer NB89 Using 3-Hydroxybenzoic Acid. The reaction was carried out similarly to NB85 using 4.00 g (28.9 mmol, 0.6l equiv) of 3-hydroxybenzoic acid, 3.632 g (19.3 mmol, 0.4 equiv) of 6-hydroxy-2-naphthoic acid, and 5.428 g (53.0 mmol, 1.06 equiv) of acetic anhydride. After acetylation, the reaction temperature was raised from 250 to 310 °C in 1 h. Acetic acid, 3.0 mL, was distilled. The sticky residue was chilled in liquid nitrogen, crushed, extracted 3 times with ether, and dried, yielding NB-89.

MALDI−TOF Measurements and Sample Preparation. MALDI−TOF measurements were carried out on a Bruker Reflex III instrument (Bruker Daltonics, Inc., Billarica, MA). A conventional nitrogen laser (337 nm) was operated at a pulse rate of 3 Hz with different attenuation values (typically in the range of 65−40%). Several acquisition methods have been used, such as delayed extraction combined with the reflectron to obtain higher resolution (3000−5000 u) for lower molecular weight oligomers (ca. < 3500 u) and linear methods covering larger molecular weight ranges (ca. 3500−200 000 u). Isotopic separation was not always possible due to the higher laser power that was necessary to apply to get reasonable spectra.

Different matrices have been used including HABA (*p*-hydroxypenylazobenzoic acid), DTH (2,6,7-trihydroxyanthracene, dithranol), HBA (2,5-dihydroxybenzoic acid), and TNB (tri-α-naphthylbenzene). The best results were obtained with DTH, so these are presented here. DTH was dissolved in CH_2Cl_2 in a concentration range of 0.1−0.2 M. In some cases, DTH was also dissolved in pentafluorophenol and was deposited onto the sample plate and dried before the sample solution was deposited on top. Several solvents and solvent combinations have been tried, but the only useful results for Vectra polymer and truncated Vectra samples have been obtained with pentafluorophenol and hexafluoro-2-propanol. In a typical experiment, 20 mg of the polymer sample was dissolved in 1000 mg of pentafluorophenol or hexafluoro-2-propanol by sonicating the solutions for 5−6 h at 30 °C. 1 μL of this highly viscous solution was deposited on the MALDI sample plate on top of the dried dithranol matrix. As suggested by Hung et al.,[16] in some cases parafilm was also used on the matrix plate to obtain less diffuse spots. Note that satisfactory results have also been obtained without using the parafilm.

Vectra A950 from Ticona (Summit, NJ) and Vectra from Aldrich (St. Louis, MO) were directly used for the MALDI−TOF analysis without any further purification.

Results and Discussion

At the onset of this study, several attempts were made to obtain authentic MALDI−TOF spectra of Vectra itself. Dithranol, 2,6,7-trihydroxyanthracene, is a widely used MALDI matrix, as is *p*-hydroxyphenylazobenzoic acid (HABA). These matrices, as well as various others, were used to prepare suitable Vectra samples for MALDI−TOF determination, but we had very limited success in mixing the polymer with the matrix. The spectra were of poor quality and only ions with lower *m/z* (<1500 Da) were detected.

In view of these negative results, polymers with more controlled structures were synthesized. Both 4-hydroxybenzoic acid and 3-hydroxybenzoic acid were used as copolymerization reaction partners with 6-hydroxy-2-naphthoic acid, resulting in the polymer samples NB85 and NB89, respectively. The 3-hydroxybenzoic acid (3-HBA) was chosen as a comonomer because it leads to a more tractable analogue of the 4-HBA all-para copolymer, the structure of the commercial Vectra. The molecular weight buildup of the polyesters was controlled by limiting the polymerization time. These polymers were found to be much more soluble in pentafluorophenol and hexafluoro-2-propanol than the commercial high molecular weight Vectra. This is especially true for the sample NB89, for which transparent solutions were obtained after several hours of sonication at 30 °C.

The MALDI−TOF spectra of NB89 and NB85 using the dithranol matrix are shown in parts a and b of Figure 1, respectively. Comparing the spectra in Figure 1a,b reveals that peaks in the spectrum of 3-HBA copolymer (NB89) are observed in a higher *m/z* region than those in the spectrum the 4-HBA copolymer (NB85). Further detailed analysis of these spectra indicates the presence of four main ion series that are denoted as series A−D (see Scheme 3 for structural details). These ion series are summarized in Table 1 up to the *m/z* ratio of 2000 Da. In the lower *m/z* range (less than ca. 1000 Da), ion series A, C, and D are present with comparable intensity. This is well demonstrated

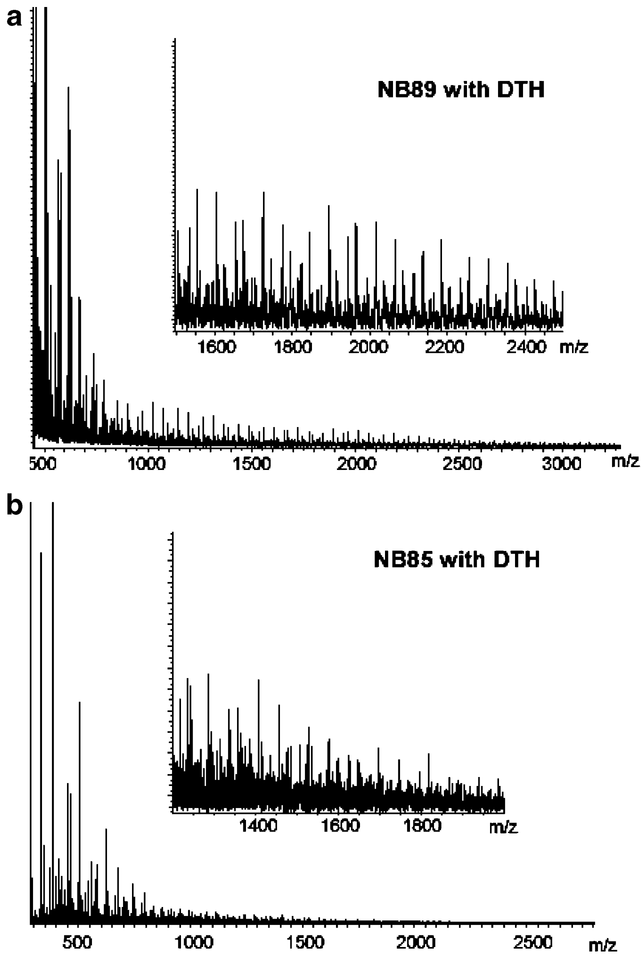
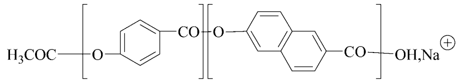


Figure 1. MALDI−TOF spectra of two "truncated" Vectra samples: (a) NB89 and (b) NB85. Both spectra were obtained with the dithranol matrix dissolved in pentafluorophenol and the samples deposited on parafilm.

Scheme 3. Main Ion Series in MALDI−TOF Spectra

Series A


Series A: $Ac(OArCO)_xOAr\text{-}COOH,Na^+$

Series B: $Ac(OArCO)_xOAr\text{-}CO\text{-}OH,H^+$

Series C: $Ac(OArCO)_xOAr\text{-}CO^+$

Series D: $H(OArCO)_xOAr\text{-}CO^+$

in Figure 2a,b showing the lower *m/z* region of the spectrum obtained for NB85. At higher *m/z* values (>1000 Da) series A becomes the dominant ion series. This is especially true for NB89, the spectra of which in the *m/z* 2800−3000 Da region are shown in Figure 3a,b. Note that these spectra show great similarities even though they were acquired for NB89 dissolved in either pentafluorophenol (Figure 3a) or hexafluoro-2-propanol (Figure 3b).

Table 1. Main Ion Series Determined by MALDI−TOF for Samples NB85 and NB89[a]

B_i	N_j	series A $Ac[B_i+N_j]OHNa^+$	series B $Ac[B_i+N_j]OHH^+$	series C $Ac[B_i+N_j]^+$	series D $H[B_i+N_j]^+$
1	0	**203**		**163**	**121**
0	1			**213**	**171**
2	0			**283**	**241**
1	1			**333**	**291**
0	2			**383**	(341)
3	0				(361)
2	1			(453)	**411**
1	2	[543]		503	461
0	3			**553**	**(511)**
3	1	[635*]		**(573)**	**531**
2	2	[663]		**623**	**(581)**
5	0	[705*]			
1	3	[713]		**673**	**631**
4	1	**733** [755*]		**693**	**651**
0	4			**723**	-
3	2	**783** [805*]		**743**	**701**
2	3	**833** [855*]		**793**	**751**
6	0	**[825*]**			
5	1	(853) [875*]			
1	4	**883** [905*]		**843**	
4	2	**903** [925*]		**863**	**821**
7	0	**[945*]**			
3	3	**953** [975*]		**913**	**871**
6	1	973 [995*]			
2	4	**1003** [1025*]		**963**	
5	2	1023 1045*		**983**	**(941)**
4	3	**1073** [1095*]		[1033]	**991**
7	1	(1093) [1115*]			
3	4	**1123** [1145*]		**1083**	
6	2	(1143)[1165*]			
2	5		(1151)		
8	1			**1173**	
5	3	**1193** [1215*]		[1153]	**1111**
10	0				(1201)
7	2			[1223]	
8	1	(1213) [1235*]			
4	4	**1243**	(1221)		
7	2	**1263** [1285*]			
3	5		(1271)		
6	3	**1313** [1335*]			(1231)
9	1	(1333) [1355*]		**1293**	
5	4	**1363** [1385*]			
8	2	(1383) [1405*]			
4	5	**1413** [1435*]	(1391)		
7	3	**1433** [1455*]			
3	6		(1441)		
6	4	**1483** [1505*]			(1401)
9	2	(1503) [1525*]		**1463**	
5	5	**1533** [1555*]	(1511)		
8	3	**1553 [1575*]**		**1513**	
4	6		(1561)		
7	4	**1603** [1625*]			
10	2	**1623 [1645*]**		**1583**	
6	5	**1653** [1675*]			
3	7		(1611)		
9	3	**1673 [1695*]**			
5	6	**1703** [1725*]	(1681)		
8	4	(1723) [1745*]			
4	7		(1731)		
11	2	(1743) [1765*]			
7	5	(1773) [1795*]			
10	3	(1793) [1815*]		(1753)	
6	6	(1823) [1845*]	(1801)		
9	4	(1843) [1865*]			
12	2	(1863) [1885*]			
5	7	(1873) [1895*]	(1851)		
8	5	(1893) [1915*]			
4	8		(1901)		
11	3	(1913) [1935*]			
7	6	(1943) [1965*]			
10	4	(1963) [1985*]			
6	7	(1993)	(1971)		

[a] Bold indicates ions found in the spectra of both polymers, parentheses indicate ions for NB89, and square brackets indicate ions for NB85. Series A−D are defined in Scheme 3 in detail. Doubly sodiated ions of series A indicated by an asterisk.

In general, the MALDI−TOF spectra contain a beautiful series of peaks corresponding to those expected for a conventional acidolysis polymerization. Series A corresponds to multiple oxybenzoyl B and oxynaphthoyl N units, carrying an acetyl group at one end and an aromatic carboxylic acid at the other complexed to Na^+, assigned as $Ac[B_i+N_j]OHNa^+$ (Scheme 3 and Table 1). In the spectra of NB85 (Figure 2a,b) doubly sodiated A-type ions $(Ac[B_i+N_j]O^-Na^+)Na$ are also present with significant intensity, and they are indicated by an asterisk in Table 1.

As mentioned above, in the lower *m/z* region (<1000 Da) the ions in series A, C, and D for NB 85 have

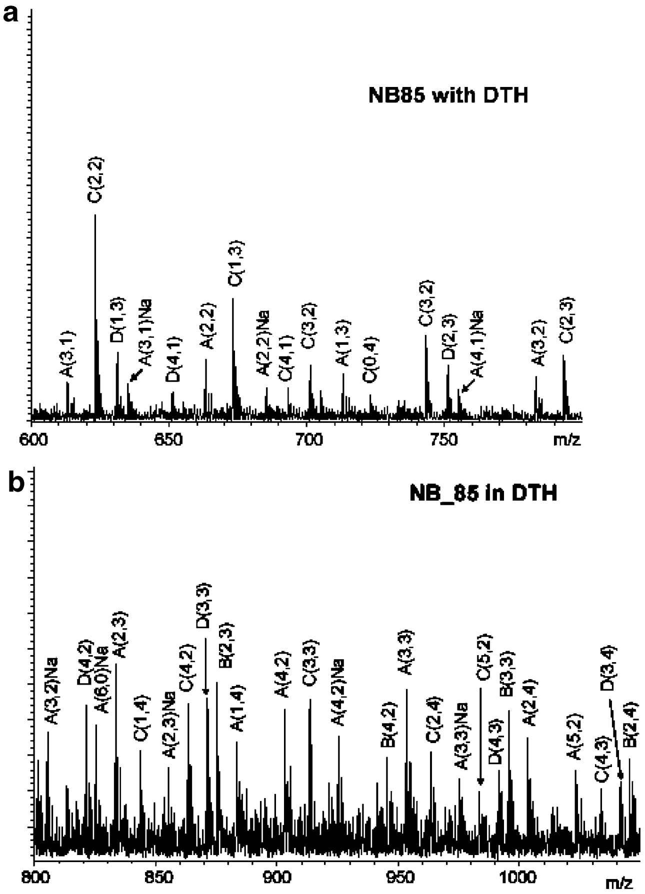
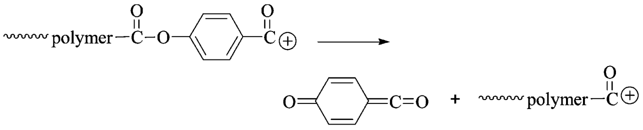


Figure 2. MALDI−TOF spectra of NB85 in the range of (a) 600−780 u and (b) 800−1050 u. The capital letters indicate the series shown in Scheme 3 and Table 1. (i, j) indicates the number of B_i and N_j copolymer units. These spectra were acquired with dithranol matrix, and the sample was dissolved in pentafluorophenol and deposited on parafilm.

Scheme 4. Depolymerization in the Para Polymer Acyl Cation



comparable intensities (Figure 2a,b). The "degraded" C and D ions are oligomeric acyl cations and can also be formed during the MALDI process. They are stabilized by the electron-donating *p*-acyloxy substituents in the all-para polymers, which is less likely in the meta-linked polymer NB89. To explain the lower molecular weights of the ions in the C and D Series, we postulate that depolymerization of the acyl cations occurs involving loss of a quinomethide molecule (Scheme 4). This quinonemethide intermediate has been detected before in the saponification of esters of *p*-hydroxybenzoic acid.[17] Depolymerization of chains with a naphthoyl acyl end group through an analogous naphthalene quinonemethide is also reasonable. Such depolymerization cannot occur for the meta-linked NB89, so the actual high oligomeric molecules can be detected in that case.

We deliberately prepared a low molecular weight copolymer NB89, and we believe that the dominant ions in the MALDI−TOF spectrum represent the authentic polymer molecules, i.e., not cleavage products. This is consistent with recent results using 3,5-diacetoxybenzoic acid-based hyperbranched polymers where no cleavage occurred in the MALDI−TOF spectra.[18,19] Nevertheless, possible fragmentation induced by MALDI is currently under investigation in our laboratory, the results of which will be published in a forthcoming paper.

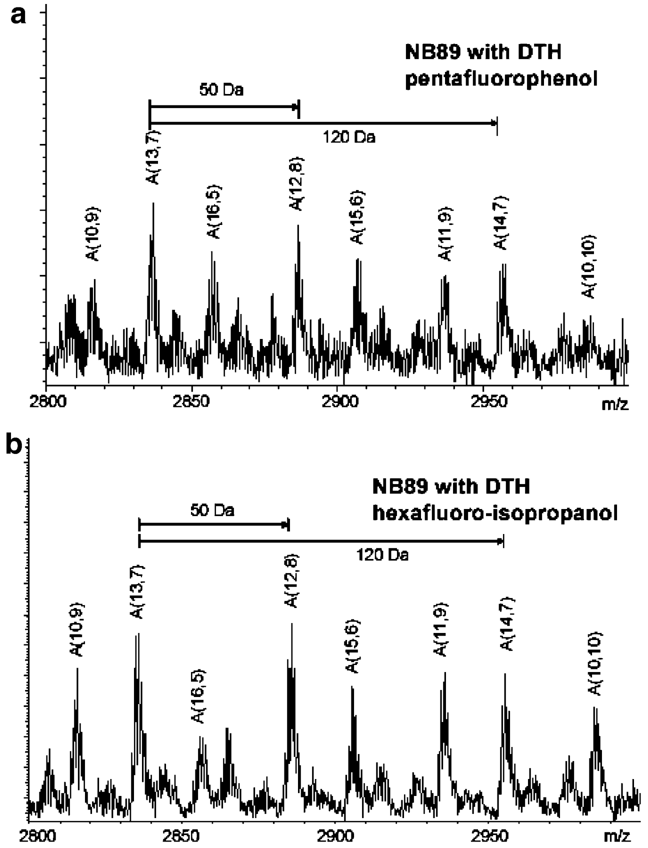


Figure 3. MALDI−TOF spectra of NB89 in the *m/z* range of *m/z* 2800−3000. In this case, the dithranol matrix was dissolved in CH_2Cl_2, and the sample was dissolved in (a) pentafluorophenol and (b) hexafluoro-2-propanol. $A(i, j)$ indicates ions corresponding to series A (Scheme 3 and Table 1) that contain B_i and N_j copolymer units.

The ion series D in the 4-HBA copolymers is of particular interest relative to the question of mechanism change. Here a phenolic hydroxyl group is at the other end of the acyl cation (Scheme 2). It arises from cleavage of ketene from the original acetyl end group. As mentioned in the Introduction, our study of the acidolysis reaction showed a mechanism change to phenolysis, involving a "degradation" reaction at both ends of the polymer chain. The loss of ketene is one of these processes, while the other end decarboxylates to form a phenyl ester. Note that a careful search of the MALDI−TOF spectra of NB85 and NB86 revealed no ions with a terminal phenyl ester group.

Accordingly the mechanistic question posed earlier has been answered: ketene loss to form a phenolic hydroxyl end group greatly precedes decarboxylation which forms phenyl esters. We caution that this conclusion applies only to the uncatalyzed reaction; potassium acetate, often used as a catalyst in these polymerizations, may alter the sequence of events.

Finally, we note that MALDI−TOF experiments allow us to monitor the copolymerization ratio. The amounts of B_i and N_j units in the NB89 polymer are shown in Figure 4. The B_i/N_j ratio quite well follows the stoichiometric ratio indicated by a solid line in Figure 4. Similar observations on the four series (A−D) have been found:

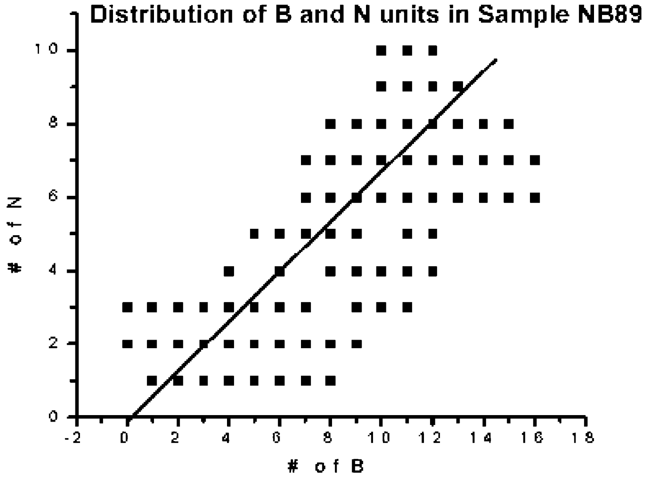


Figure 4. Distribution of monomer units in sample NB89 for the ions belonging to series A. The solid line indicates the stoichiometric ratio of B/N (3:2) used in the polymerizations.

(i) they are mixtures of B and N units, (ii) no long sequences of either B or N are observed with significant intensity, so they must have comparable reactivity, and (iii) we cannot specify the sequence distribution of B and N in the peaks reported.

Conclusions

Although MALDI−TOF has been and will certainly be widely and successfully used for the analysis of synthetic polymers, in some cases, the sample preparation could be a painful and time-consuming process. Furthermore, the quality of the spectra and their interpretation may depend on sample preparation. We believe that the experience we had obtained with such a highly intractable and formerly not studied polymer, Vectra (and its truncated analogues), will be useful for other scientists working with related polymers. A critical review focusing on the limitations of MALDI−TOF spectroscopic technique in synthetic polymer analyses would be of great need and would certainly be welcomed by polymer chemists.

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