CNR-ICTP

MALDI-TOF Analysis of Complex Materials Formed in the Melt-mixing and in the Degradation of Polymers

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MALDI-TOF OF POLYMERS

- Detection of Intact Molecules
- Very High Sensitivity
- High Resolution
- MS/MS

APPLICATIONS

- Molar Mass Determination
- Copolymer Analysis
- End Groups Determination
  - Mechanisms of Polymer Degradation
  - Mechanisms of Synthesis

Analysis of Copolymers by MS

- **1986** Project Begins
- **1987** **FAB-MS** of Synthetic Polymers
- **1989** Partial degradation methodology
- **1991** Theoretical Mass Spectra of Copolymers
- **1993** **MALDI-TOF** of “Intact” Copolymers

FAB-MS Analysis Needs Oligomers

Copolymer Chain

-A-A-B|-A-B-B-A-|A-B-A-

Partial Degradation

-A-A-B + A-B-B-A+ A-B-A-

Molecular Weight Reduction by Partial Degradation

1. **Hydrolysis**
2. **Methanolysis**
3. **Aminolysis**
4. **Photolysis**
5. **Pyrolysis**
6. **Ozonolysis**

MODELING PROCESS BASED ON CHAIN STATISTICS

1. CHOICE OF DISTRIBUTION MODELS

A NUMBER OF DIFFERENT DISTRIBUTION MODELS CAN BE CONSIDERED, OLIGOMERS ABUNDANCES CAN BE GENERATED ACCORDING TO EACH MODEL (BERNOULLIAN, MARKOFFIAN 1° AND 2°, SEQUENTIAL)

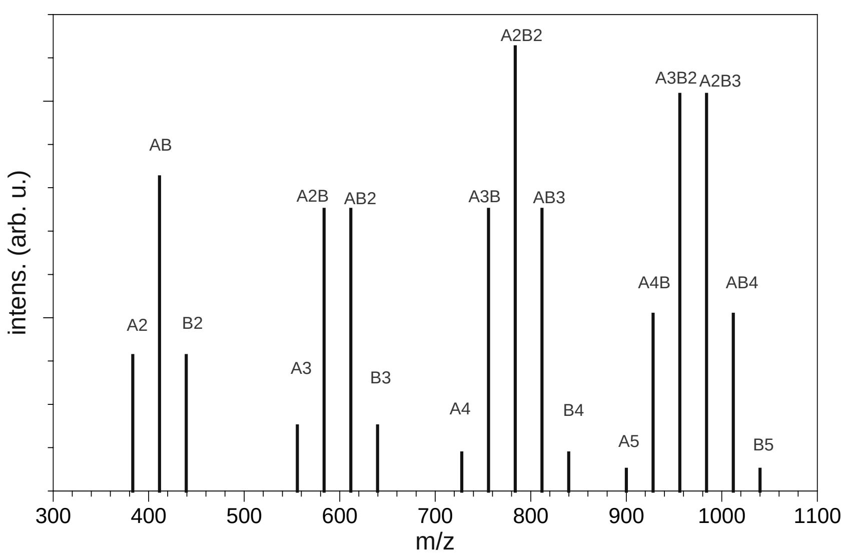
2 THEORETICAL MASS SPECTRA

GENERATE THEORICAL MASS SPECTRA FOR A SPECIFIC COPOLYMER SEQUENCE BY ASSUMING PEAKS INTENSITIES EQUAL TO RELATIVE OLIGOMER ABUNDANCES, AND APPLYING THE APPROPRIATE CONVOLUTION AND MULTIPLICITY RULES

3 ITERATION AND BEST FIT MINIMIZATION

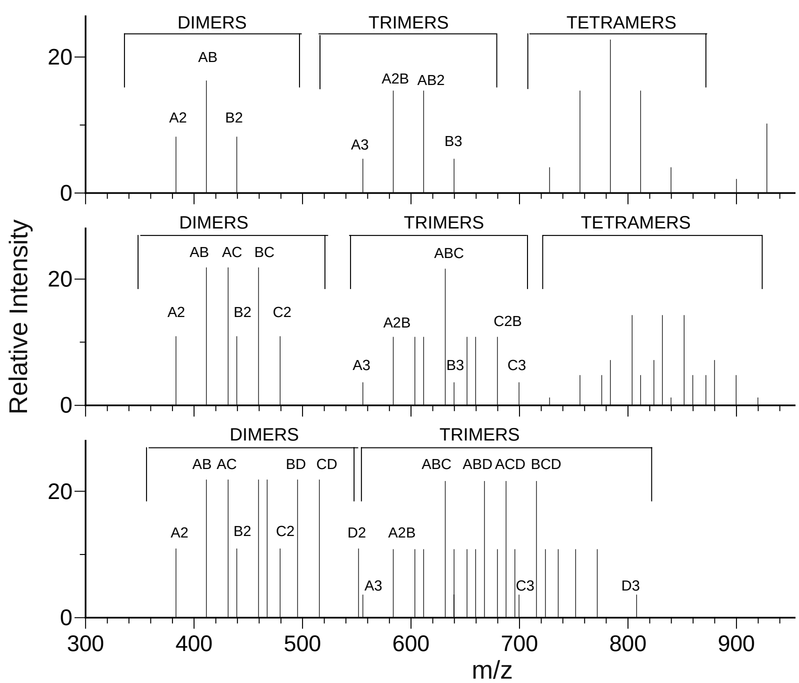
A SERIES OF THEORETICAL MASS SPECTRA ARE ORIGINATED AND, COMPARING THE EXPERIMENTAL MS INTENSITIES WITH THOSE CALCULATED FOR A SPECIFIC MODEL, THE MOST LIKELY COPOLYMER MICROSTRUCTURE AND COMPOSITION CAN BE DETERMINED

Number of MS peaks (n+1)
random AB copolymer (1:1)



Number of peaks expected for two, three ad four components copolymers

Oligomers	AB	ABC	ABCD
2-mers	3	6	10
3-mers	4	10	20
4-mers	5	15	35
5-mers	6	21	56
6-mers	7	28	84
7-mers	8	36	120
8-mers	9	45	165
9-mers	10	55	220
10-mer	11	66	286
11-mers	12	78	364
12-mers	13	91	455
13-mers	14	105	560
14-mers	15	120	680
15-mers	16	136	816
16-mers	17	153	969



A= 172

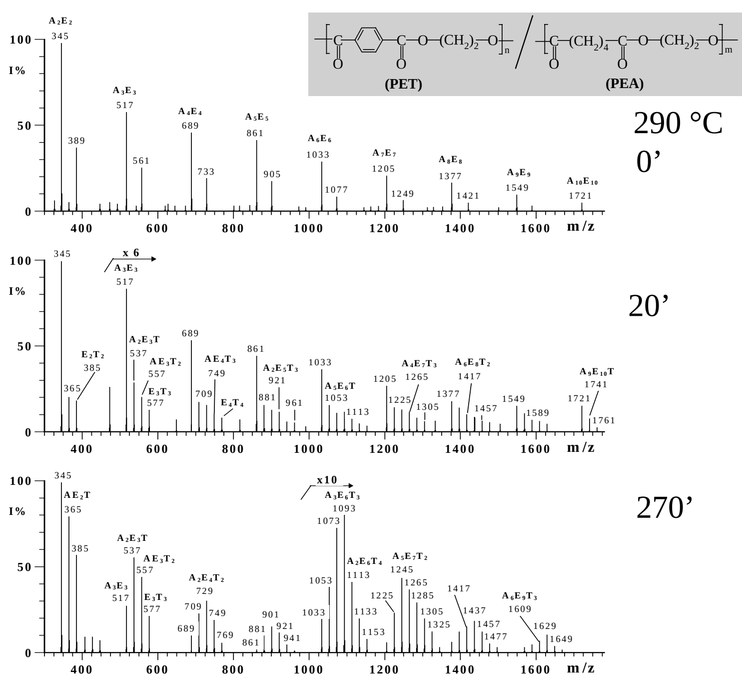
B=200

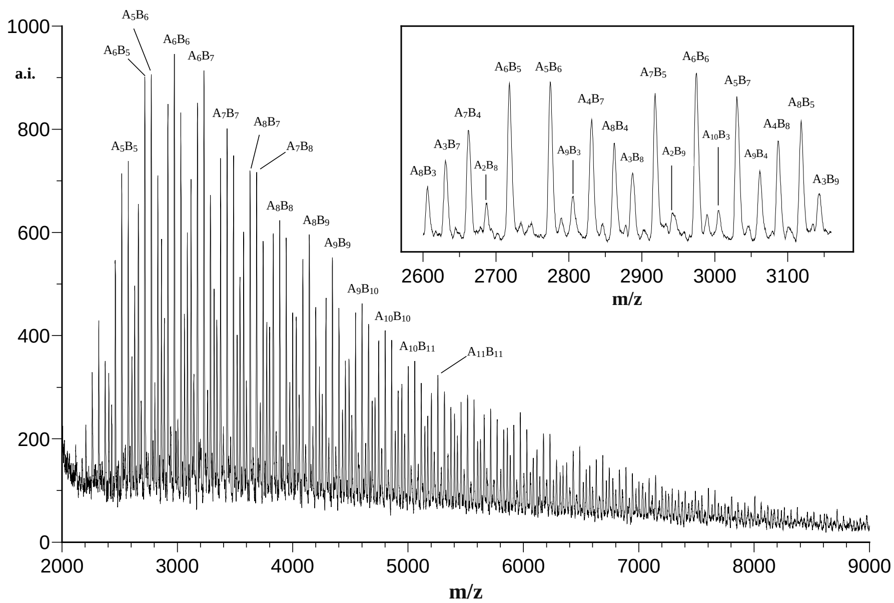
C=220

g/mol

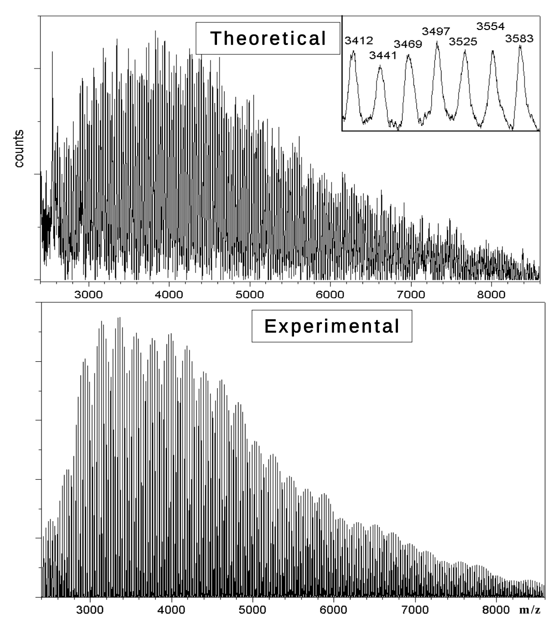
Composition for a AB copolymer

Oligomers		Formula
Monomers	C_1^A	**I(A) / { I(A) + I(B) }**
Dimers	C_2^A	$\{2I(A_2) + I(AB)\}$ / $\{2I(A_2) + 2I(AB) + 2I(B_2)\}$
Trimers	C_3^A	$\{3I(A_3) + 2I(A_2B) + I(AB_2)\}$ / $\{3I(A_3) + 3I(A_2B) + 3I(AB_2) + 3I(B_3)\}$
Tetramers	C_4^A	$\{4I(A_4) + 3I(A_3B) + 2I(A_2B_2) + I(AB_3)\}$/ $\{4I(A_4) + 4I(A_3B) + 4I(A_2B_2) + 4I(AB_3)\ 4I(B_4)\}$





MALDI-TOF spectrum of butylene adipate (A)/sebacate (B) copolymer.

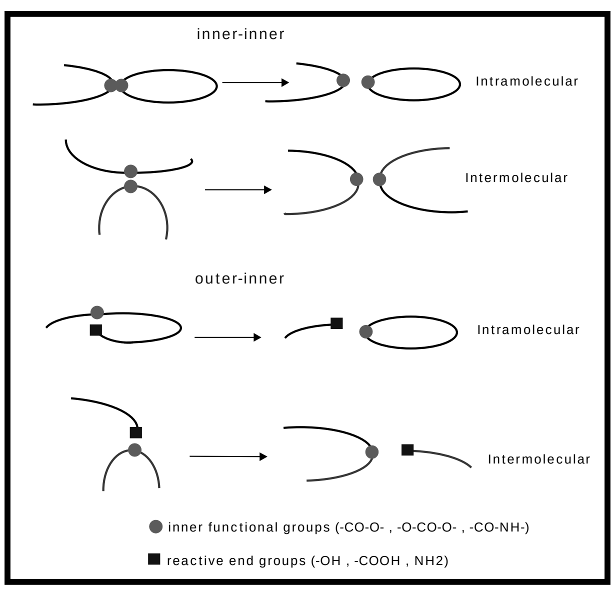


MALDI-TOF Spectra of a three components copolymer (BSu-BAd-Bse)

MALDI-TOF Analysis of Copolymers formed
in the melt mixing of polymer mixtures

- End groups deternination
- Copolymer microstructure

Schematic representation of exchange reaction mechanisms occurring
in the melt-mixing of polymers containing reactive functional groups



A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

\+

B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B

HOMOPOLYMERS

↓

A-A-A-A-A-A-A-A-A-A-A-A-A-A-B-B-B-B

\+

B-B-B-B-B-B-B-B-B-B-B-B-B-B-A-A-A-A

TWO BLOCK COPOLYMERS

↓

A-A-A-B-B-A-A-A-A-A-B-B-B-A-A-B-B-B

\+

B-B-B-A-A-B-B-B-B-B-A-A-A-B-B-A-A-A

TWO SEGMENTED COPOLYMERS

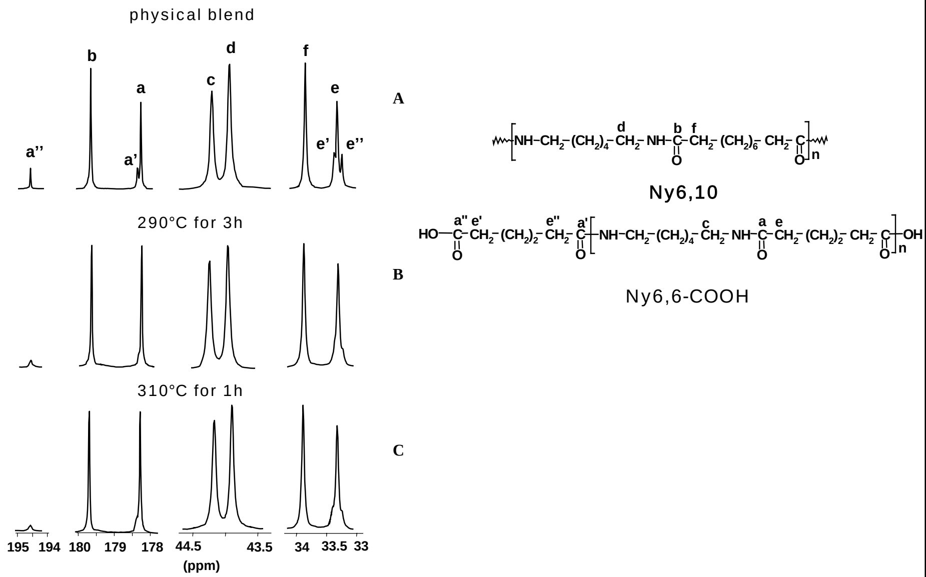
↓

B-B-A-B-A-A-B-B-A-A-A-B-B-B-A-A-B-A

RANDOM COPOLYMERS

Blends illustrated in this presentation

- Nylon 6,6 – Nylon 6,10
- PET – Nylon 6
- PBT – Nylon 6



^{13}C-NMR spectra of Ny6,6-COOH and Ny6,10 equimolar mixtures

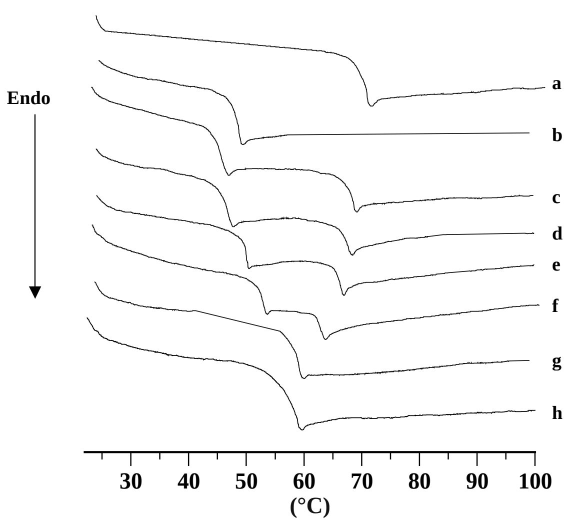
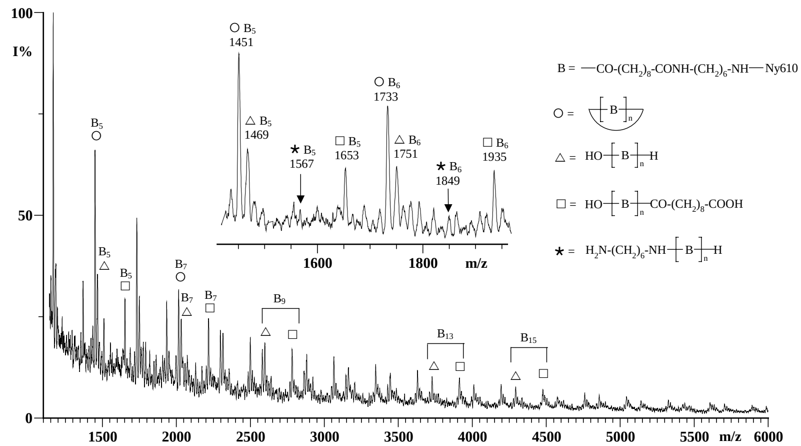
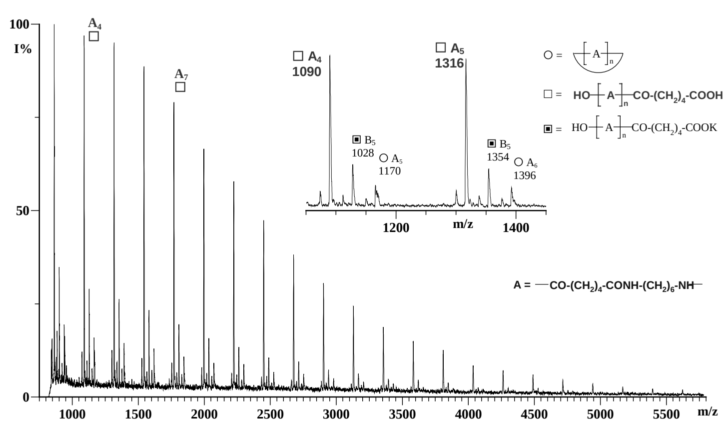


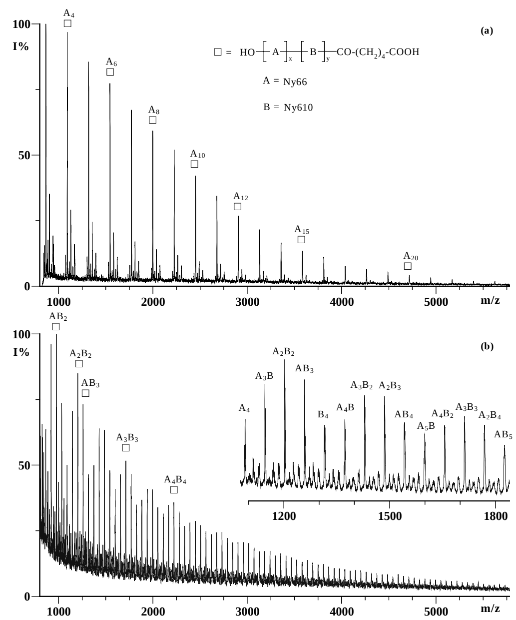
Figure 7. DSC curves in the range 25-100°C (recorded at 10°C/min in heating mode) of (a) Ny6,10, (b) Ny6,6-COOH, and Ny6,6-COOH/Ny6,10 reacted at 290°C for: (c) 0 min, (d) 5 min, (e) 10 min, (f) 15 min, (g) 30 min, and (h) 60 min.

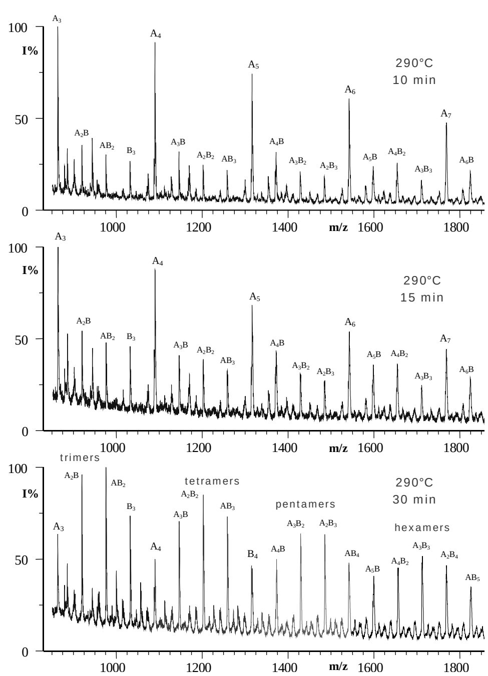


MALDI-TOF mass spectrum of high molar mass Ny610 sample



MALDI-TOF mass spectrum of Ny66-COOH


(a)
(b)
A = Ny66
B = Ny610
HO-[A]x-[B]y-CO-(CH2)4-COOH
I%
m/z
A4
A6
A8
A10
A12
A15
A20
AB2
A2B2
AB3
A3B3
A4B4
A3B
B4
A4B
A3B2
A2B3
AB4
A5B
A4B2
A2B4
AB5


290°C
10 min
290°C
15 min
290°C
30 min
trimers
tetramers
pentamers
hexamers
I%
m/z

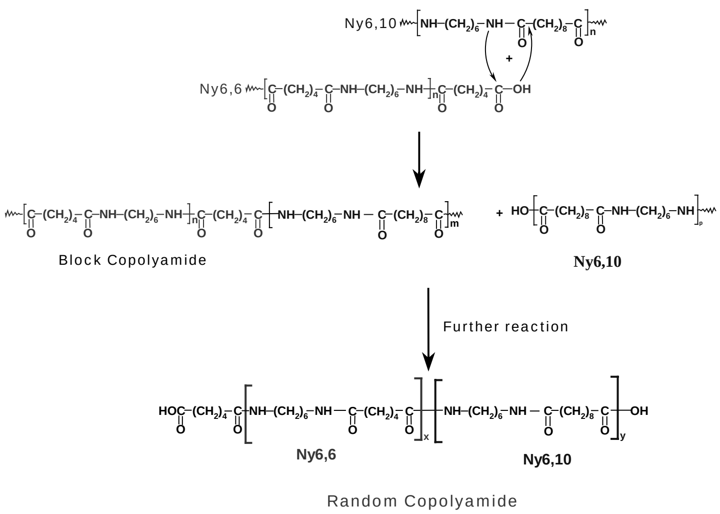


Table 3. Results of the Analysis of MALDI−TOF Spectra of Ny6,6-COOH/Ny6,10 and Ny6,6/Ny6,10 Melt-Mixed Blends Using the MACO4 Program

heating time (min)	P matrix[a] ($P_{AA}/P_{AB}/P_{BA}/P_{BB}$)	extent of exchange[a]	composition[a] $C_{Ny6,6}/C_{Ny6,10}$	degree of randomness[a]	av. sequence length[a] $n_{Ny6,6}/n_{Ny6,10}$	agreement factor[a]
10	0.75/0.25/0.40/0.60	70	62/38	0.70	4.0/2.5	20
15	0.7/0.3/0.43/0.57	73	59/41	0.73	3.3/2.3	20
30	0.60/0.40/0.40/0.60	80	50/50	0.80	2.5/2.5	11
60	0.58/0.42/0.40/0.60	81	49/51	0.82	2.4/2.5	11
180	0.57/0.43/0.4/0.51	83	48/52	0.83	2.3/2.5	14
150[b]	0.81/0.19/0.24/0.76	43	56/44	0.43	5.3/4.1	20

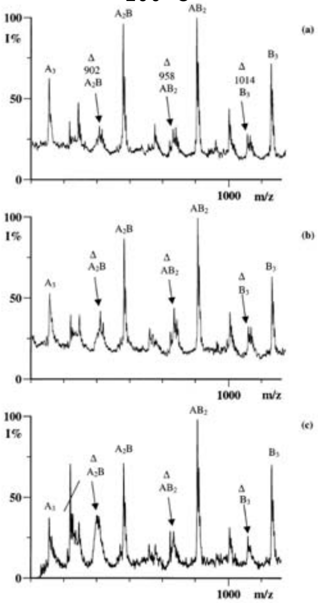
[a] Calculated according to ref 25. [b] Mixture of high molar mass Ny6,6 and Ny6,10 with a low amount of carboxyl chain ends.

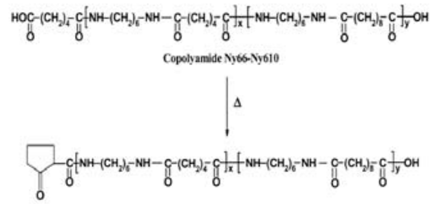
290 °C

30 min

60 min

180 min



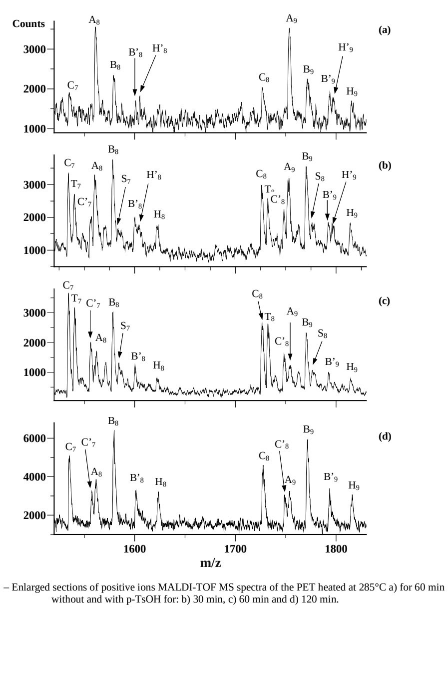


Analysis of products formed in the melt-mixing of PET and Ny6

- PET and Ny6 blends are not compatible and generate a two phases materials by mixing in the melt.
- PET and Ny6 blends became compatible in the presence of hydrated p-toluene-Sulfonic acid (p-T-SO_3H).
- In the literature p-T-SO_3H is considered as a trans-amidation catalyst.
- In the presence of anidrous p-T-SO_3H the PET/Ny6 exchange reaction is not observed.

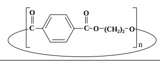
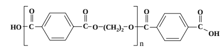
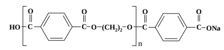
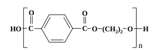
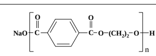
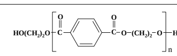
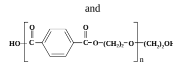
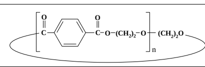
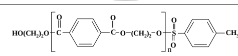
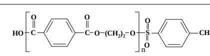
Table 1. Viscosity (η_{inh}), Average Molar Mass (M_v), and Weight-Loss Data of PET and Ny6 Samples Isothermally Heated with and without TsOH

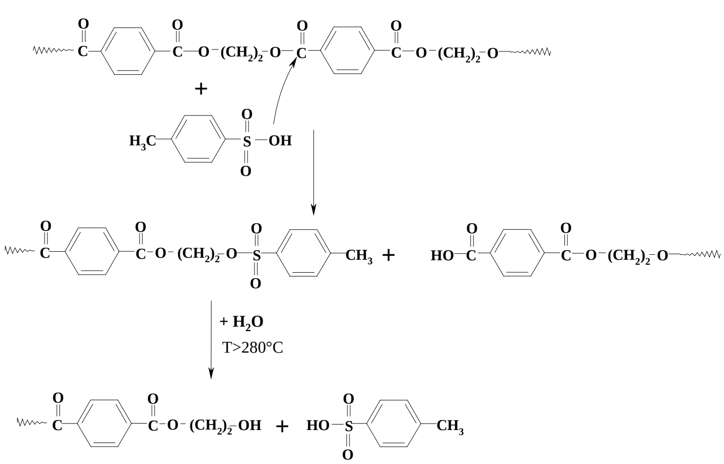
	Thermal Treatment				
Sample	T (°C)	t (min)	TsOH (wt %)	η_{inh}(dL/g)[a]	M_v[b]
PET	—	—		0.56	44,000
	285	60	—	0.57	44,500
	285	120	—	0.56	44,000
	270	150	0.5	0.53	41,100
	285	30	0.5	0.43	30,700
	285	60	0.5	0.39	26,900
	285	120	0.5	0.33	21,600
Ny6	—	—	—	0.696	30,300
	285	60	—	0.631	28,500
	285	120	—	0.58	23,500
	285	120	0.5	0.584	24,000



– Enlarged sections of positive ions MALDI-TOF MS spectra of the PET heated at 285°C a) for 60 min without and with p-TsOH for: b) 30 min, c) 60 min and d) 120 min.

Table 2 - Assignments of the mass peaks present in the enlarged sections of the MALDI spectra of heated PET samples at 285 °C, with and without TsOH, reported in Figure 1.

Species	Structure	M+Na$^+$ (n)	M$^-$ (n)
A		1560 (8) 1752 (9)	--- ---
B		1534 (7) 1726 (8)	1510 (7) 1702 (8)
B'		1556 (7) 1748 (8)	1532 (7) 1724 (8)
C		1578 (8) 1770 (9)	1554 (8) 1746 (9)
C'		1600 (8) 1792 (9)	--- ---
H	 and 	1622 (8) 1814 (9)	--- ---
H'		1604 (8) 1796 (9)	--- ---
S		1584 (7) 1776 (8)	--- ---
T		1540 (7) 1732 (8)	1516 (7) 1708 (8)



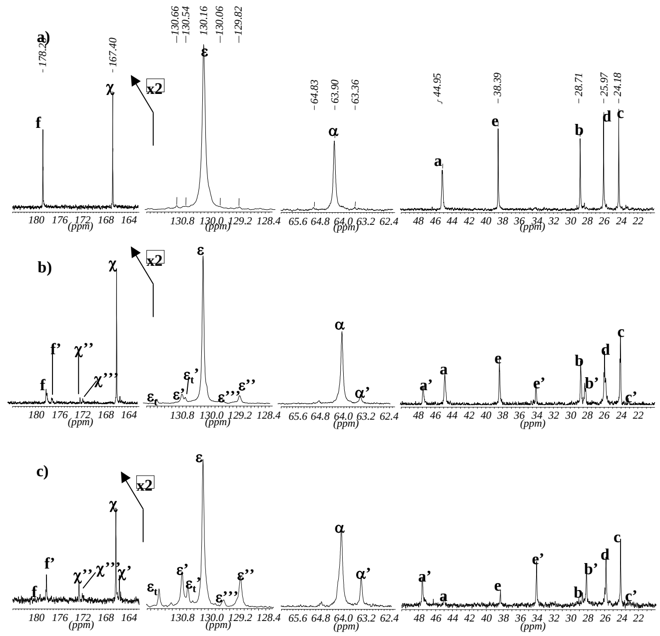
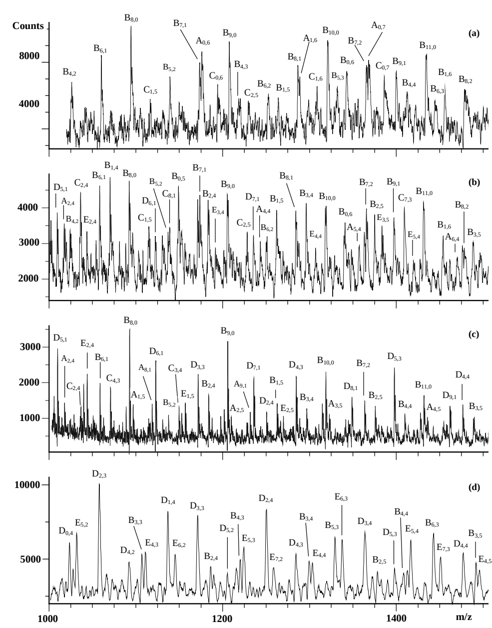
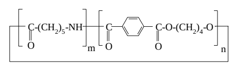
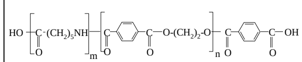
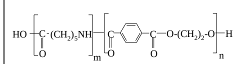
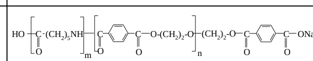
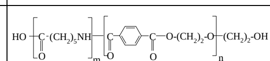


Figure 2- ^{13}C-NMR spectra of the Ny6PET physical blend (a) and of the Ny6/PET blends melt mixed with TsOH at 285 °C for 120 min (b) and 180 min (c).



– Enlarged sections of positive ions MALDI spectra of the Ny6/PET blends of melt mixed at 285°C without TsOH for 120 min(a), and with TsOH (0.5%w) for: 20 min (b), 120 min(c) and 180 min (d).

Table 5: Structural assignments of peaks displayed in the MALDI-TOF mass spectra of the melt mixed Ny6/PET blends reported in Figure 4.

Species	Structures	$[M+Na]^+$ (m,n)
$A_{n,m}$		1018(2,4); 1041(9,0); 1097(1,5); 1120(8,1); 1131(3,4); 1154(10,0); 1176(0,6); 1210(2,5); 1233(9,1); 1244(4,4); 1267(11,0); 1323(3,5); 1346(10,1); 1357(5,4); 1368(0,7) 1380(12,0); 1436(4,5); 1470(6,4); 1493(13,0)
$B_{n,m}$		1025(4,2); 1060(6,1); 1071(1,4); 1094(8,0); 1105(3,3); 1139(5,2); 1150(0,5); 1173(7,1); 1184(2,4); 1207(9,0); 1218(4,3); 1252(6,2); 1263(1,5); 1286(8,1); 1297(3,4); 1320(10,0); 1331(5,3); 1342(0,6); 1365(7,2); 1376(2,5); 1399(9,1); 1410(4,4); 1433(11,0); 1444(7,3); 1455(1,6); 1478(8,2); 1489(3,5)
$C_{n,m}$		1036(2,4); 1059(9,0); 1068(4,3); 1104(6,2); 1115(1,5); 1138(8,1); 1147(3,4); 1172(10,0); 1194(0,6) 1217(7,2); 1228(2,5); 1285(11,0); 1296(6,3); 1307(1,6); 1341(3,5); 1386(0,7); 1398(12,0); 1409(7,3)
$D_{n,m}$		1013(5,1); 1024(0,4); 1058(2,3); 1092(4,2); 1126(6,1); 1137(1,4); 1171(3,3); 1205(5,2); 1239(7,1); 1250(2,4); 1284(4,3); 1352(8,1); 1363(3,4); 1397(5,3); 1465(9,1); 1476(4,4)
$E_{n,m}$		1035(5,2); 1080(2,4); 1114(4,3); 1148(6,2); 1159(1,5); 1193(3,4); 1227(5,3); 1261(7,2); 1272(2,5); 1306(4,4); 1340(6,3); 1385(3,5); 1419(5,4); 1453(7,3); 1498(4,5)

MALDI Analysis

Table 7: Yield of copolyesteramide, Copolymer composition, Pmatrix elements, average sequence lengths of the E-T and CL-CL units, and degree of randomness (B) of the Ny6/PET copolyesteramides formed during the melt mixing at 285°C for different times of equimolar Ny6/PET blends with and without TsOH, calculated from MALDI mass spectra using the statistical MACO4 program.

Time (min)	TsOH %w	Yield[a] %	Composition C_{CL}/C_{ET}	P-matrix elements				Molar fraction of dimers[b]				Average sequence lengths		
				P_{CL-CL}	P_{CL-ET}	P_{ET-CL}	P_{ET-ET}	F_{CL-CL}	F_{CL-ET}	F_{ET-CL}	F_{ET-ET}	CL-CL	E-T	B[c]
120	----[d]	51	55/45	0.95	0.05	0.06	0.94	0.52	0.03	0.03	0.42	22	18	0.10
10	0.5	54	58/42	0.94	0.06	0.08	0.92	0.55	0.03	0.03	0.39	38	32	0.13
20	0.5	64	54/46	0.93	0.07	0.09	0.91	0.50	0.04	0.04	0.42	27	23	0.16
60	0.5	80	51/49	0.90	0.10	0.10	0.90	0.46	0.05	0.05	0.44	11	10	0.18
120	0.5	92	48/52	0.82	0.18	0.17	0.83	0.39	0.09	0.09	0.43	5	4	0.35
180	0.5	100	48/52	0.38	0.62	0.58	0.42	0.18	0.30	0.30	0.22	1.6	1.7	1.20

a) yield of copolyesteramide formed in the blends after heating

b) $F_{CL-CL} = P_{CL-CL} \cdot C_{CL}$; $F_{CL-ET} = P_{CL-ET} \cdot C_{CL}$; $F_{ET-CL} = P_{ET-CL} \cdot C_{ET}$; $F_{ET-ET} = P_{ET-ET} \cdot C_{ET}$;

c) $B = P_{ET-CL} + P_{CL-ET}$;

d) Melt mixed without TsOH.

^{13}C-NMR Analysis

Molar fraction of dyads, average sequence lengths and degree of randomness (B) calculated from ^{13}C-NMR spectra of equimolar Ny6/PET blends melt mixed at 285 °C for different times with and without TsOH .

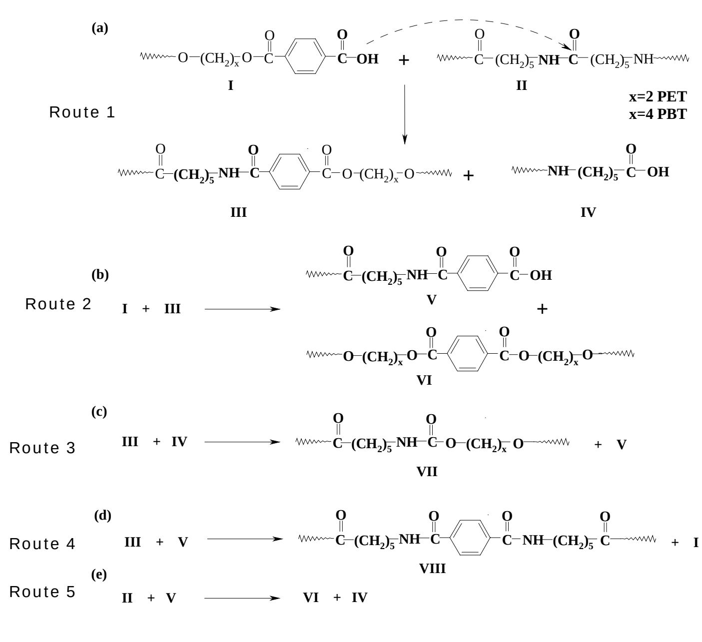
Time (min)	TsOH **%w**	Molar fraction of dyads[(a)] F_{CL-CL}	F_{CL-E}	F_{CL-T}	F_{E-T}	Average sequence lengths[(b)] E-T	CL-CL	B[(c)]
0	**---**	**0.5**	**---**	**---**	**0.5**	**-**	**-**	**-**
120	**---[(d)]**	**0.44**	**0.03**	**0.06**	**0.47**	**8.8**	**8.3**	**0.18**
10	**0.5**	**0.47**	**0.015**	**0.03**	**0.49**	**17.2**	**16.7**	**0.09**
20	**0.5**	**0.46**	**0.02**	**0.04**	**0.48**	**14.3**	**14.3**	**0.11**
60	**0.5**	**0.45**	**0.05**	**0.05**	**0.45**	**10.1**	**10**	**0.18**
120	**0.5**	**0.37**	**0.09**	**0.13**	**0.41**	**4.15**	**3.84**	**0.44**
180	**0.5**	**0.14**	**0.24**	**0.34**	**0.29**	**1.85**	**1.4**	**1.15**

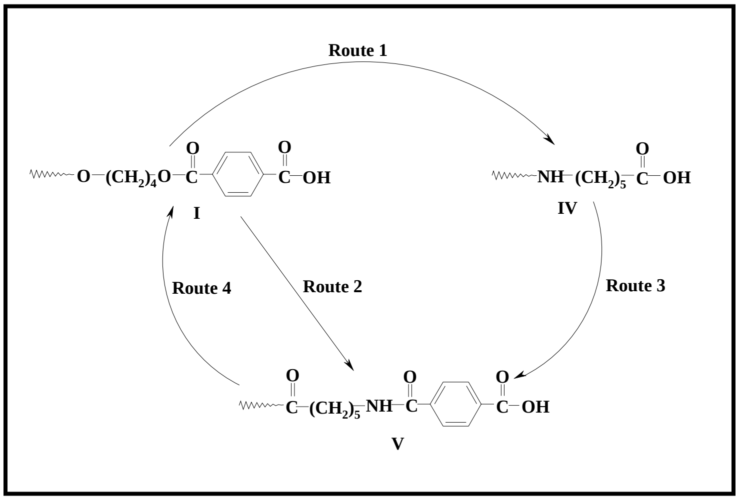
a) **$F_{E-T} = (A_{\alpha} - 1/2A_{\alpha'}/A_{\alpha}+A_{\alpha'}) \bullet C_{E-T}$; $F_{CL-E} = (2\,A_{\alpha'}/\,A_{\alpha}+A_{\alpha'}) \bullet C_{E-T}$; $F_{CL-CL} = (A_a/A_a+A_{a'}) \bullet C_{CL}$; $F_{CL-T} = (A_{b'}/A_b+A_{b'}) \bullet C_{CL}$; where A_{α}, $A_{\alpha'}$, A_a, $A_{a'}$, A_b, and $A_{b'}$ indicate the area of the peaks α, α', a, a', b, and b', respectively, in the ^{13}C-NMR spectra. The molar concentration of E-T (C_{E-T}) and CL (C_{CL}) units is both 0.5 mol.**

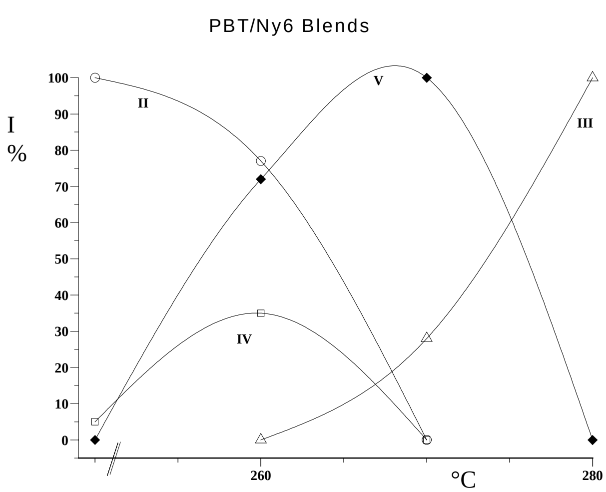
b) **E-T = $1/F_{CL-E}$; CL-CL = $1/F_{CL-T}$;**

c) **B = F_{CL-T}/C_{E-T} + F_{CL-E}/C_{CL} ;**

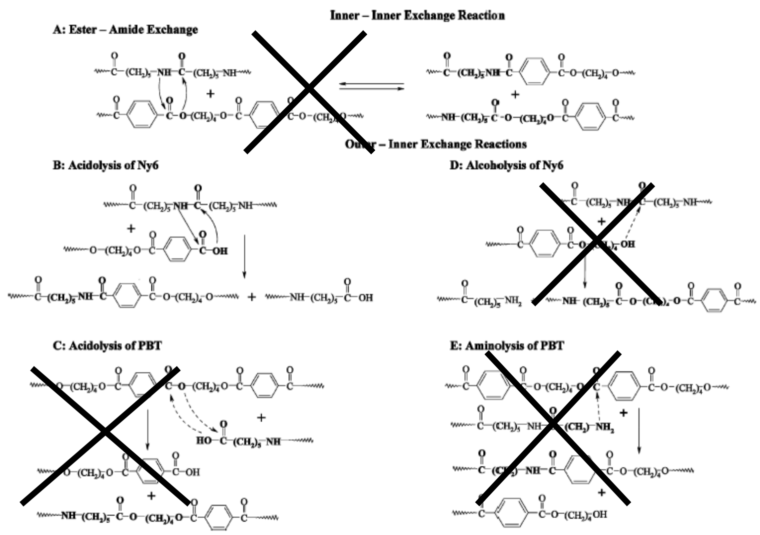
d) **Melt mixed without TsOH.**







Normalized intensity/temperature profiles of some specific peaks, in the MALDI spectra, corresponding to species II, III, IV and V.



MALDI-TOF Analysis of Copolymers formed
in the melt mixing of polymer mixtures

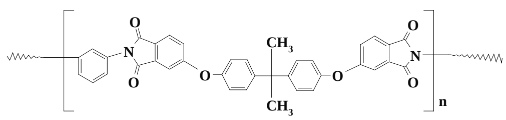
- ❑ End groups deternination
  - Exchange Mechanisms
  - Role of Catalysts
  - Role of inner and outer reactive functional groups
  - Role of reaction parameters: time and temperature
- ❑ Copolymer microstructure
  - Copolymer composition
  - Copolymer average sequence lengths
  - Degree of randomness
  - Exent of reaction

Photodegradation Mechanisms

Nylon 6

$$\left[-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CO- \right]_n$$

Ultem



Nylon 6

$$\left[-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CO- \right]_n$$

Remarkable information on the photo oxidation of Nylon 6 and Nylon 66 has been provided, in the past, mainly by UV and IR spectroscopy and by wet chemistry methods

Experimental Details

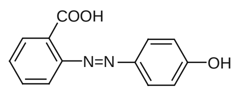
Films of Nylon6 with a thickness of 10 µm were exposed on a "QUV" apparatus at 60 °C to UV radiation up to 19 days.

The irradiance of the UV lamps (UVA 340 lamps) has a broad band with a maximum at 340 nm.

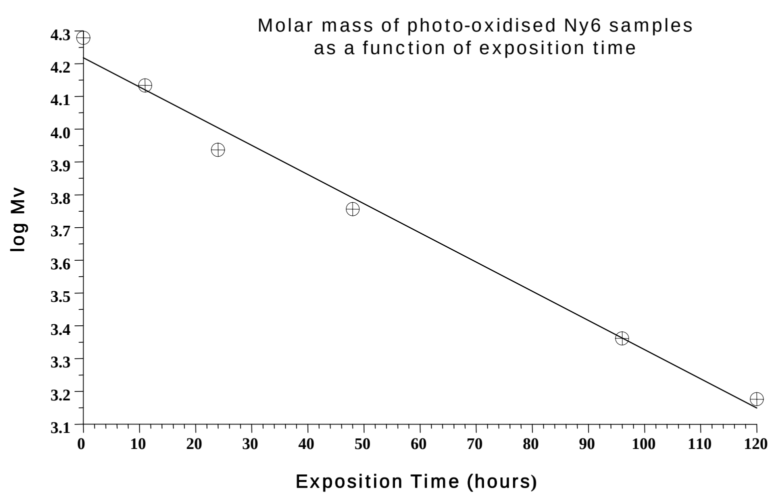
The samples for the MALDI analyses were prepared by mixing adequate volumes of the matrix solution (HABA, 0.1 M in TFE) and polymer solution (2mg/mL in TFE) to obtain a 1:1 or 1:3 ratio (sample/matrix)v/v.

1 µL of a 0.1 M solution of sodium trifluoroacetate (NaTFA) in TFE was added to aid cationization.

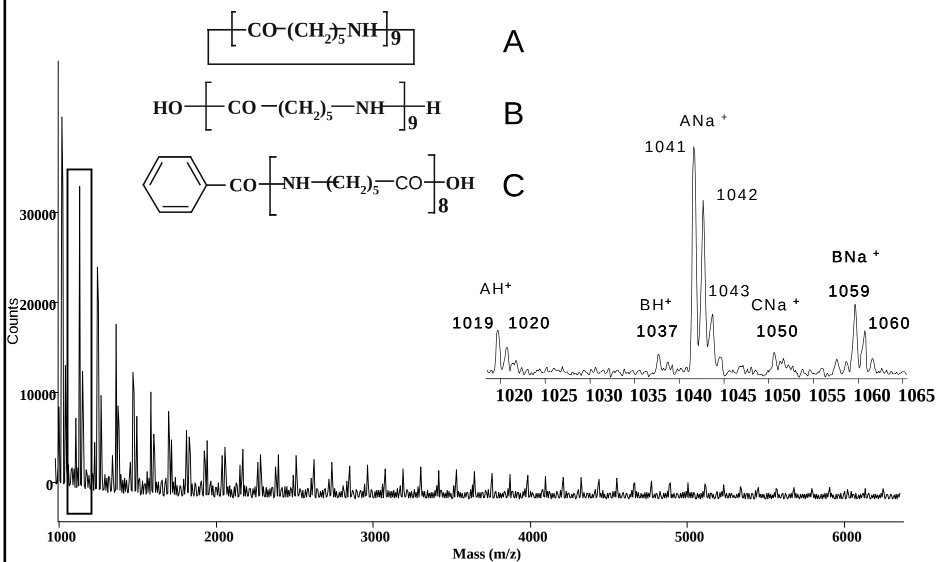
1 µL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.



HABA

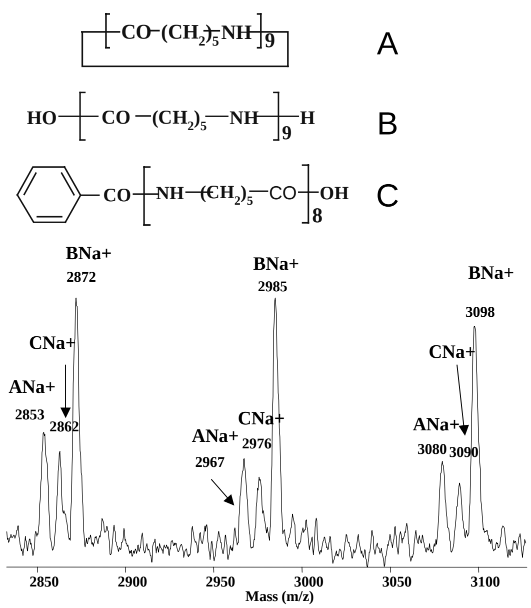


CNR-ICTP

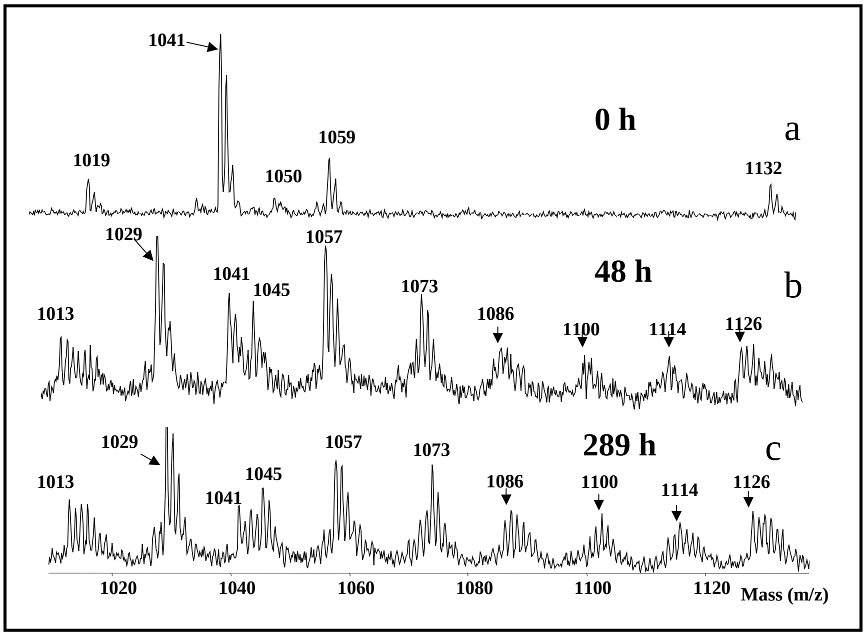


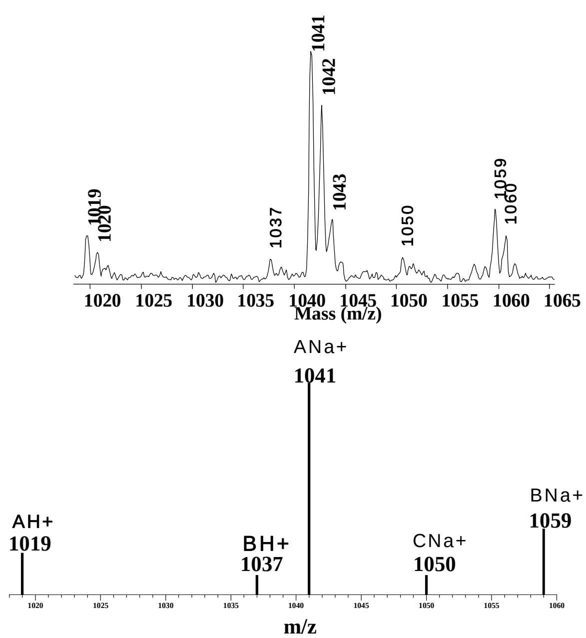
MALDI-TOF mass spectrum of Ny6

CNR-ICTP



MALDI-TOF mass spectrum of Ny6 in the range 2800-3100





MALDI-TOF mass spectrum of Ny 6 after the deisotoping procedure.

Deisotopized MALDI-TOF Mass Spectrum, in the mass range 1010-1120Da of Ny6 sample photo-oxidized for 289 hours.

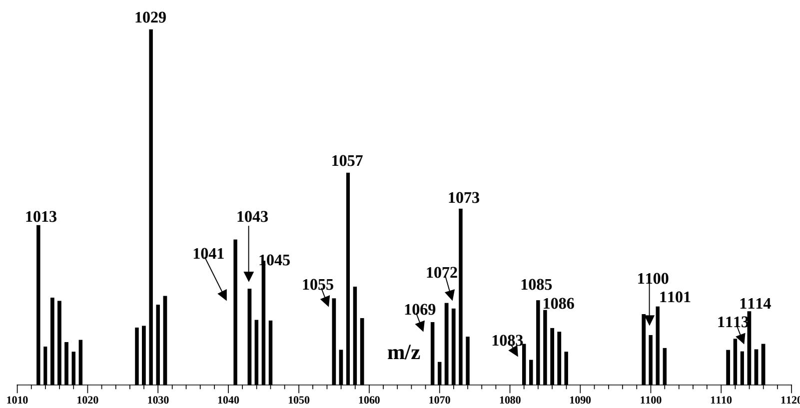


Photo-oxidation processes [a]	Structures	M+Na$^+$
B—E	$H_2C{=}CH-(CH_2)_3-HN[CO-(CH_2)_5-NH]_8H$	1013
B—A	$H_3C-(CH_2)_4-HN[CO-(CH_2)_5-NH]_7CO-(CH_2)_4-CHO$	1014
C—A	$H_2C{=}HC-(CH_2)_2-HN[CO-(CH_2)_5-NH]_7CO-(CH_2)_4-COOH$	
B—E	$H_3C-(CH_2)_4-HN[CO-(CH_2)_5-NH]_8H$	1015
C—A	$H_3C-(CH_2)_3-HN[CO-(CH_2)_5-NH]CO-(CH_2)_4-COOH$	1016
B—E	$OHC-HC{=}HC-(CH_2)_2-HN[CO-(CH_2)_5-NH]_8H$	1027
B—A	$OHC-(CH_2)_4-HN[CO-(CH_2)_5-NH]_7CO-(CH_2)_4-CHO$	1028
B—E	$OHC-(CH_2)_4-HN[CO-(CH_2)_5-NH]_8H$	1029
B—A	$H_3C-(CH_2)_4-HN[CO-(CH_2)_5-NH]_7CO-(CH_2)_4-COOH$	1030
Cyclic Ny6	$[CO-(CH_2)_5-NH]_9$ (cyclic)	1041

C—C	$H_3C-(CH_2)_3-HN-[CO-(CH_2)_5-NH]_8-CO-CH_3$	1043
B-A-A	$H_3C-(CH_2)_3-CO-HN-[CO-(CH_2)_5-NH]_7-CO-(CH_2)_4-COOH$	1044
B—E	$HOOC-(CH_2)_4-HN-[CO-(CH_2)_5-NH]_8-H$	1045
A—A	$H_2N-[CO-(CH_2)_5-NH]_8-CO-CH_2-CH_2-CH{=}CH-CHO$	1055
E—A	$HO-[CO-(CH_2)_5-NH]_8-CO-CH_2-CH_2-CH{=}CH-CHO$	1056
A—A B—C	$H_2N-[CO-(CH_2)_5-NH]_8-CO-(CH_2)_4-CHO$ $H_3C-(CH_2)_4-HN-[CO-(CH_2)_5-NH]_8-CO-CH_3$	1057
A—E E—A	$H_2N-[CO-(CH_2)_5-NH]_9-H$ $HO-[CO-(CH_2)_5-NH]_8-CO-(CH_2)_4-CHO$	1058
Linear Ny 6	$HO-[CO-(CH_2)_5-NH]_9-H$	1059
B—C	$OHC-CH{=}HC-(CH_2)_2-HN-[CO-(CH_2)_5-NH]_8-CO-CH_3$	1069
E-A-A	$HO-[OC-(CH_2)_4-CO-NH]_2-[CO-(CH_2)_5-NH]_6-CO-(CH_2)_2-CH{=}CH-CHO$	1070
B—C	$OHC-(CH_2)_4-HN-[CO-(CH_2)_5-NH]_8-CO-CH_3$	1071

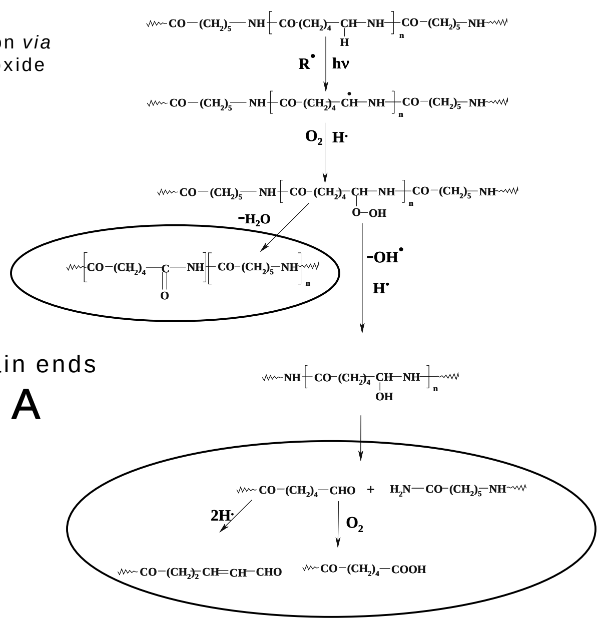
A—A E-A-A	$H_2N-[CO-(CH_2)_5-NH]_8-CO-(CH_2)_4-CO-NH_2$ $HO-[OC-(CH_2)_4-CO-NH][CO-(CH_2)_5-NH]_7-CO-(CH_2)_4-CHO$	1072
A—A	$H_2N-[CO-(CH_2)_5-NH]_8-CO-(CH_2)_4-COOH$	1073
E—A	$HO-[CO-(CH_2)_5-NH]_8-CO-(CH_2)_4-COOH$	1074
B-A-C	$OHC-CH{=}CH-(CH_2)_2-NH-[CO-(CH_2)_4-CO-NH]-[CO-(CH_2)_5-NH]_7-CO-CH_3$	1083
B-A-C	$OHC-(CH_2)_4-NH-[CO-(CH_2)_4-CO-NH][CO-(CH_2)_5-NH]_7-CO-CH_3$	1085
A—B	$H_2N-[CO-(CH_2)_5-NH]_9-CHO$	1086
B—C E—B	$HOOC-(CH_2)_4-HN-[CO-(CH_2)_5-NH]_8-CO-CH_3$ $HO-[CO-(CH_2)_5-NH]_9-CHO$	1087
E-A-A	$HO-[OC-(CH_2)_4-CO-NH][CO-(CH_2)_5-NH]_7-CO-(CH_2)_4-COOH$	1088
A—C	$H_2N-[CO-(CH_2)_5-NH]_9-CO-CH_3$	1100
E—C	$HO-[CO-(CH_2)_5-NH]_9-CO-CH_3$	1101
E-A-A	$HO-[OC-(CH_2)_4-CO-NH]_2-[CO-(CH_2)_5-NH]_6-CO-(CH_2)_4-COOH$	1102

C—A	$H_2C{=}CH{-}(CH_2)_2{-}NH{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO$	1111
C—E	$H_2C{=}CH{-}(CH_2)_2{-}NH{-}[CO{-}(CH_2)_5{-}NH]_9{-}H$	1112
C—A	$H_3C{-}(CH_2)_3{-}NH{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO$	1113
C—E	$H_3C{-}(CH_2)_3{-}NH{-}[CO{-}(CH_2)_5{-}NH]_9{-}H$	1114
E-A-C	$HO{-}[CO{-}(CH_2)_4{-}CO{-}NH]{-}[CO{-}(CH_2)_5{-}NH]_8{-}COCH_3$	1115

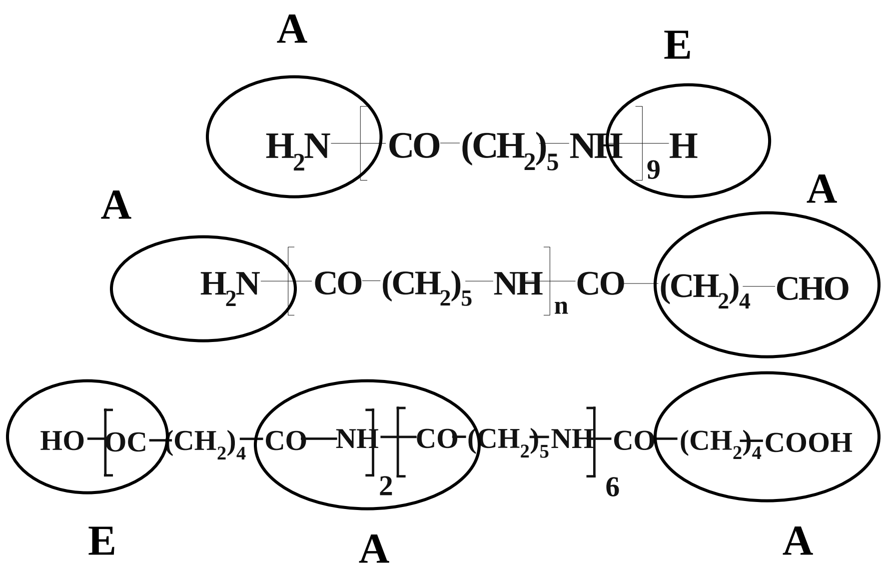
a) Terminal groups originated by specific photo-oxidation processes:

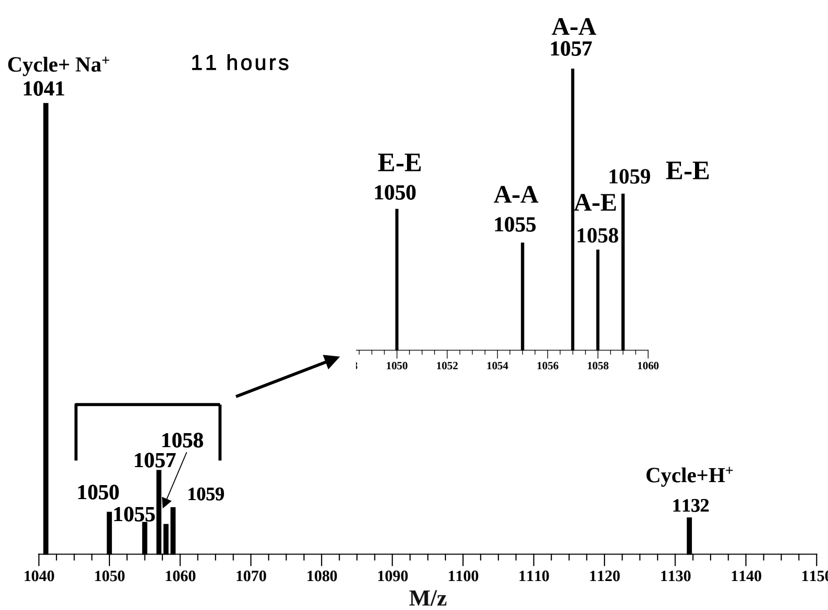
A= Hydroperoxides
B= Norrish I
C= Norrish II
E= End Groups of the unexposed Nylon6

Degradation *via* Hydroperoxide

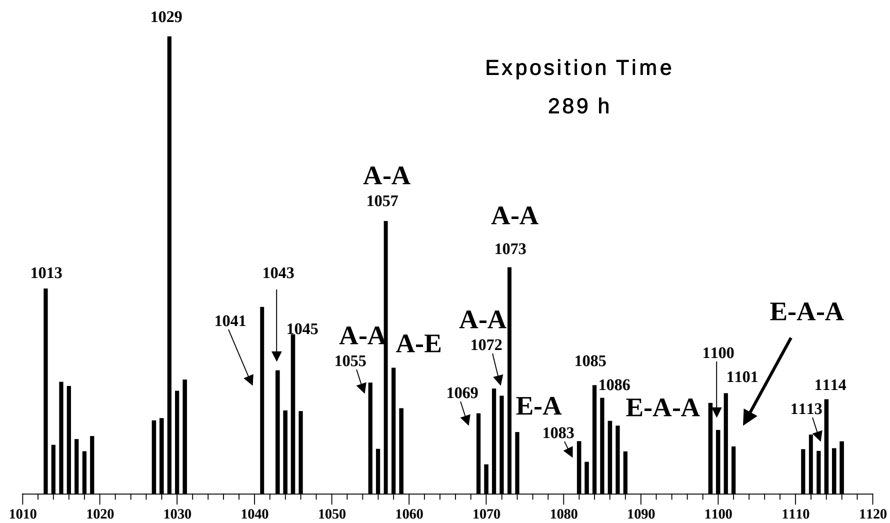


chain ends
A

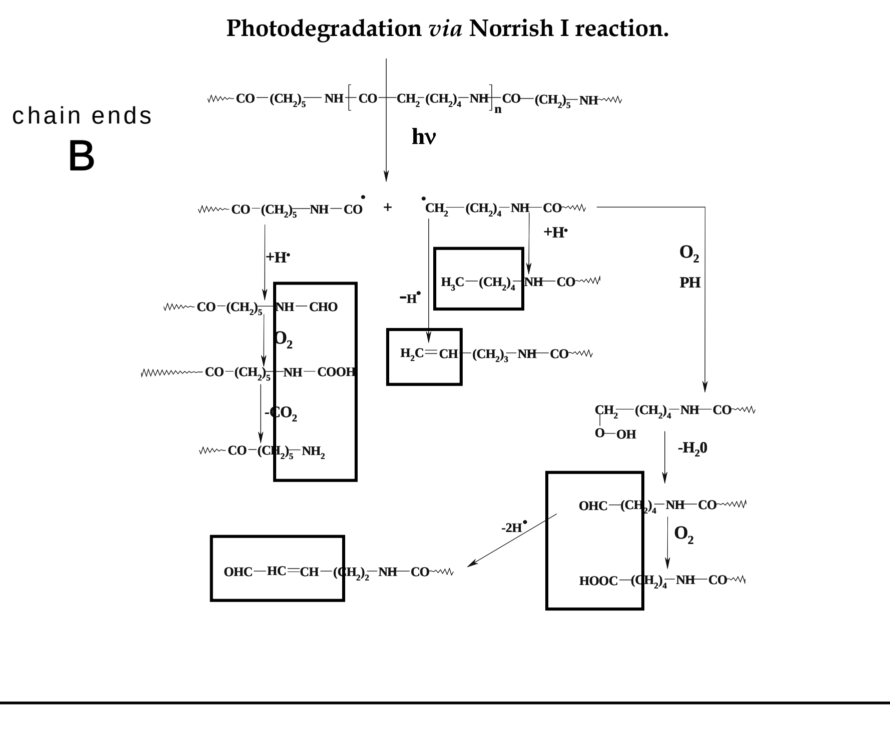




Deisotopized MALDI-TOF Mass Spectrum, in the mass range 1010-1120Da of Ny6 sample photo-oxidized for 11 hours.

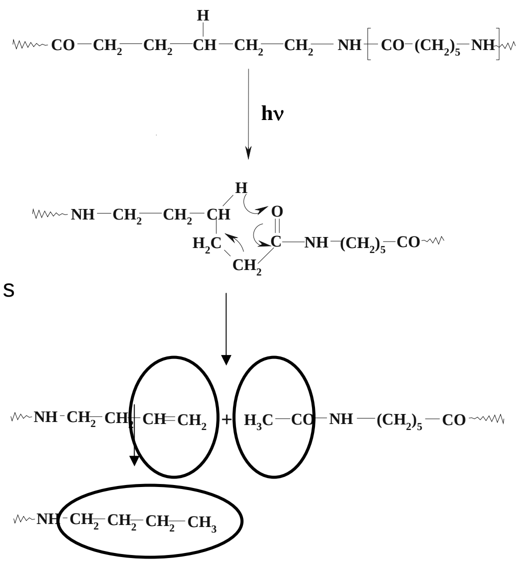


Exposition Time
289 h
1029
1013
1041
1043
1045
A-A
1055
A-A
1057
A-E
A-A
1073
A-A
1072
1069
E-A
1083
1085
1086
E-A-A
1100
1101
E-A-A
1113
1114
1010
1020
1030
1040
1050
1060
1070
1080
1090
1100
1110
1120



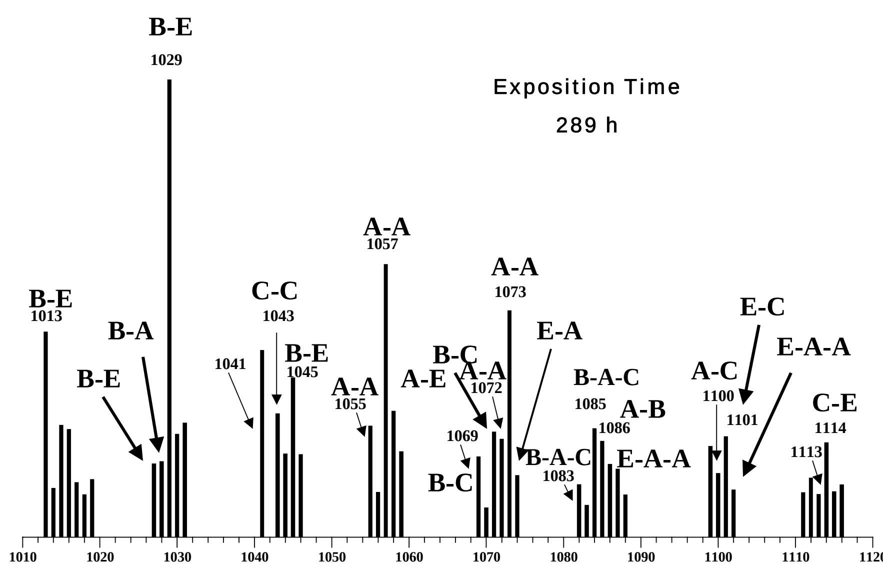
Photodegradation via Norrish I reaction.
chain ends
B
hν
+H•
O2
-CO2
-H•
+H•
O2
PH
-H20
O2
-2H•

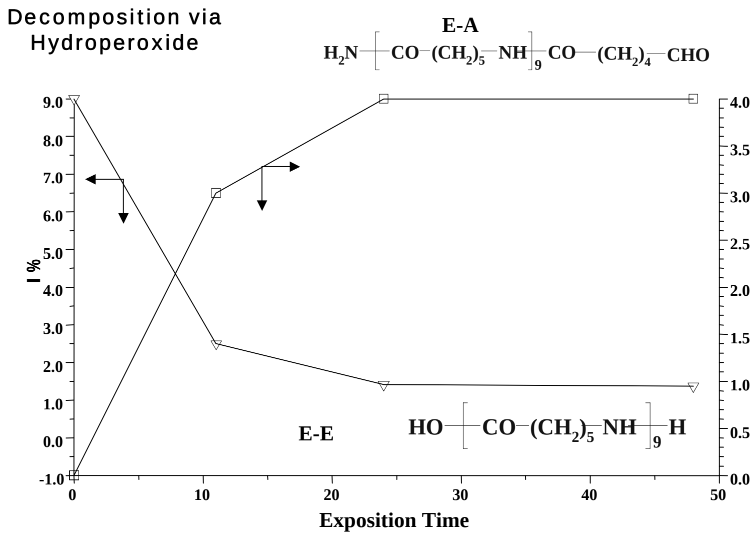
Photodegradation *via* Norrish II reaction



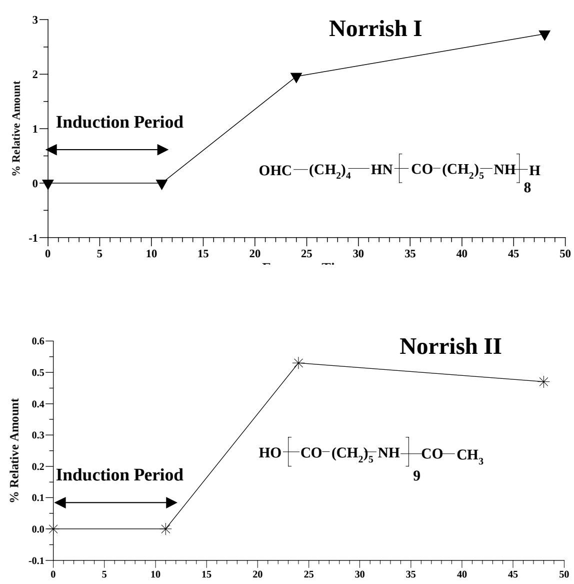
chain ends

C

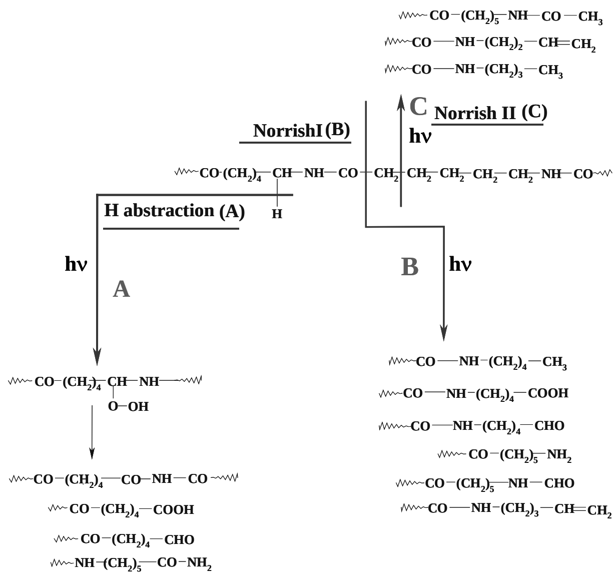




Relative amount vs exposition time of species at m/z 1058 and 1059, as obtained from the MALDI spectra of photo-oxidized Ny6 sample

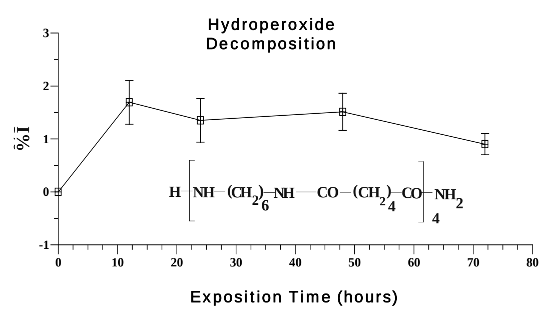


Relative amount vs exposition time of species at m/z 1029 and 1100, as obtained from the MALDI spectra of photo-oxidized Ny6 sample

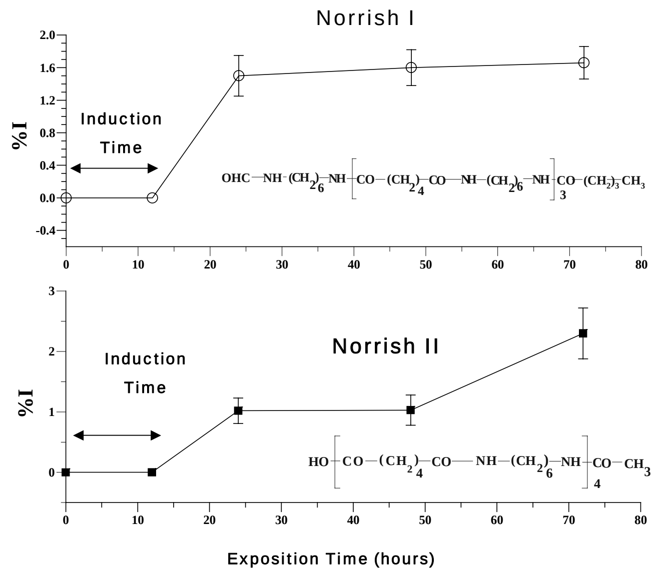


Overall Photo-oxidation Processes in Ny6.

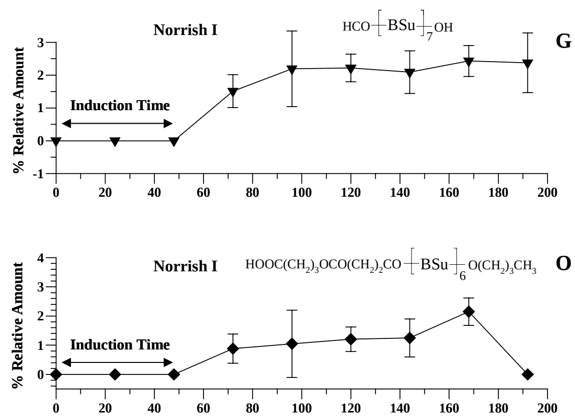
Nylon 66 Photo-oxidation



Nylon 66 Photo-oxidation



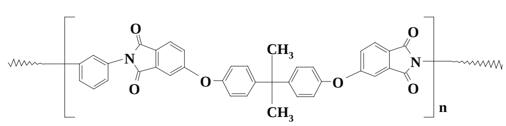
Polyesters

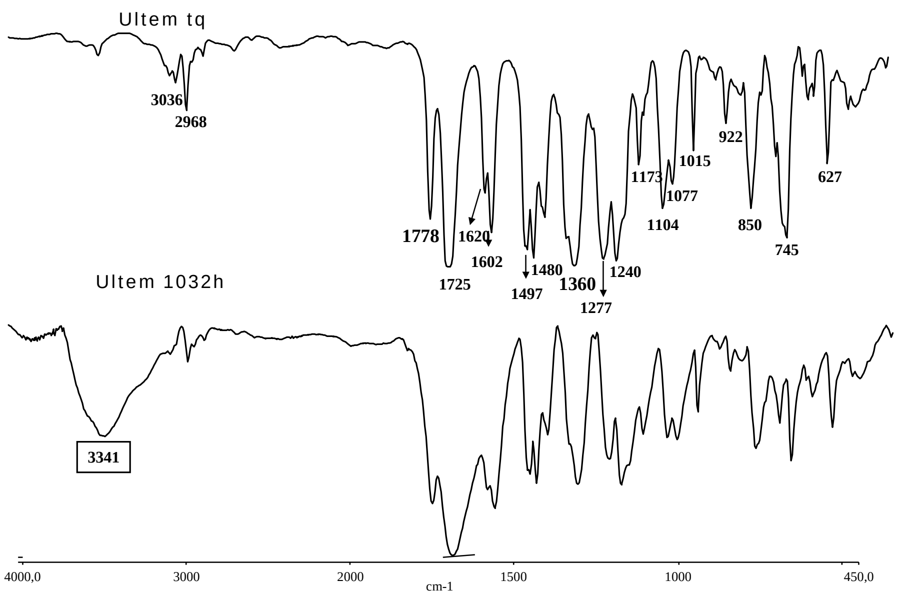


B-E $OHC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H$

A-A $H_2N{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO$

Photo-oxidation of Ultem





FT-IR spectra of ULTEM samples Photo-oxidised at 60°C for 0 and 1032 hours

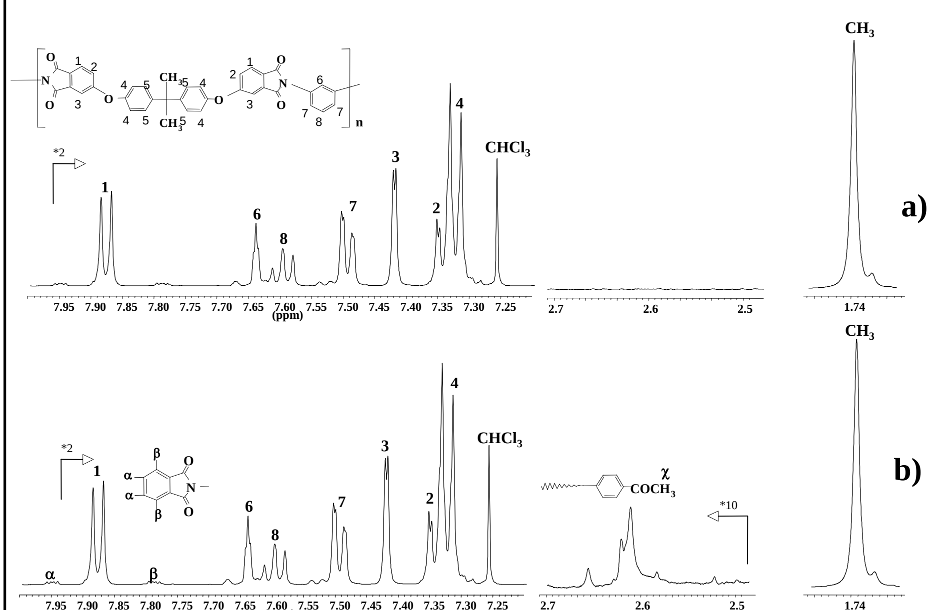
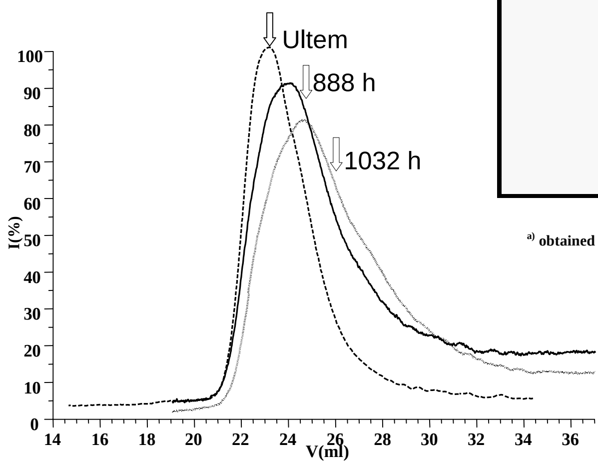
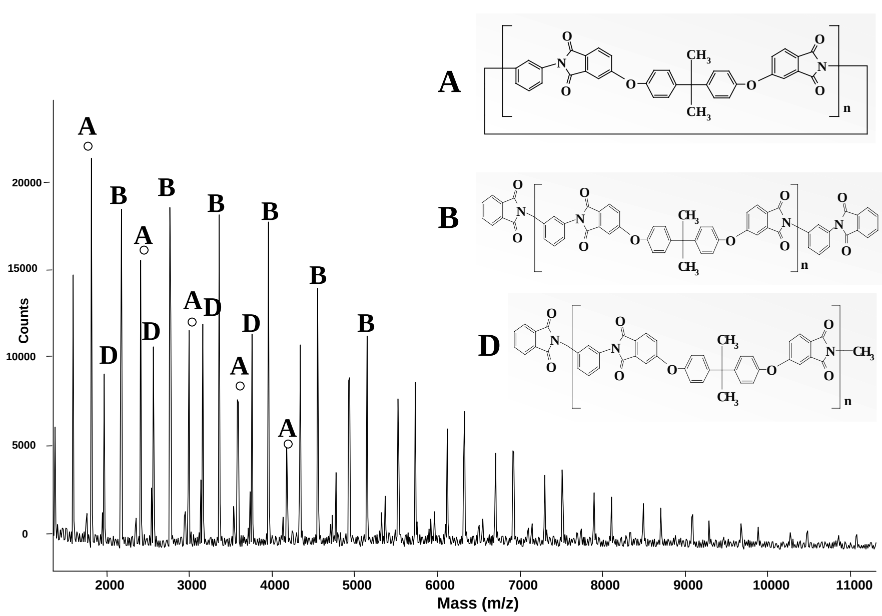


Figure 3. ^{1}H-NMR spectra of PEI Samples Photo-oxidised at 60°C for 0 and 1032 hours

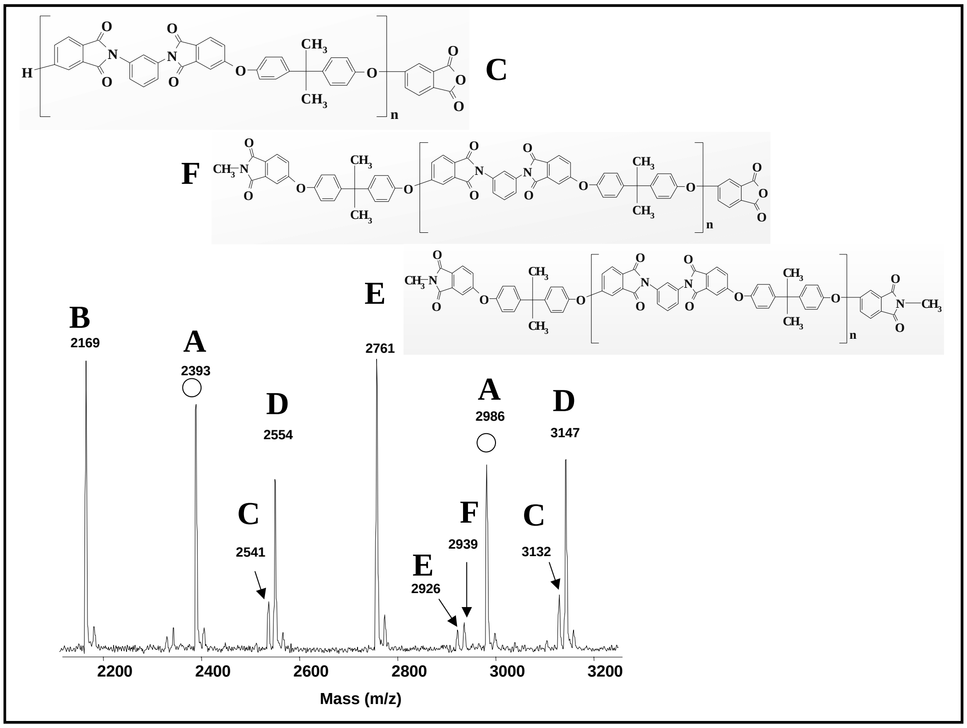


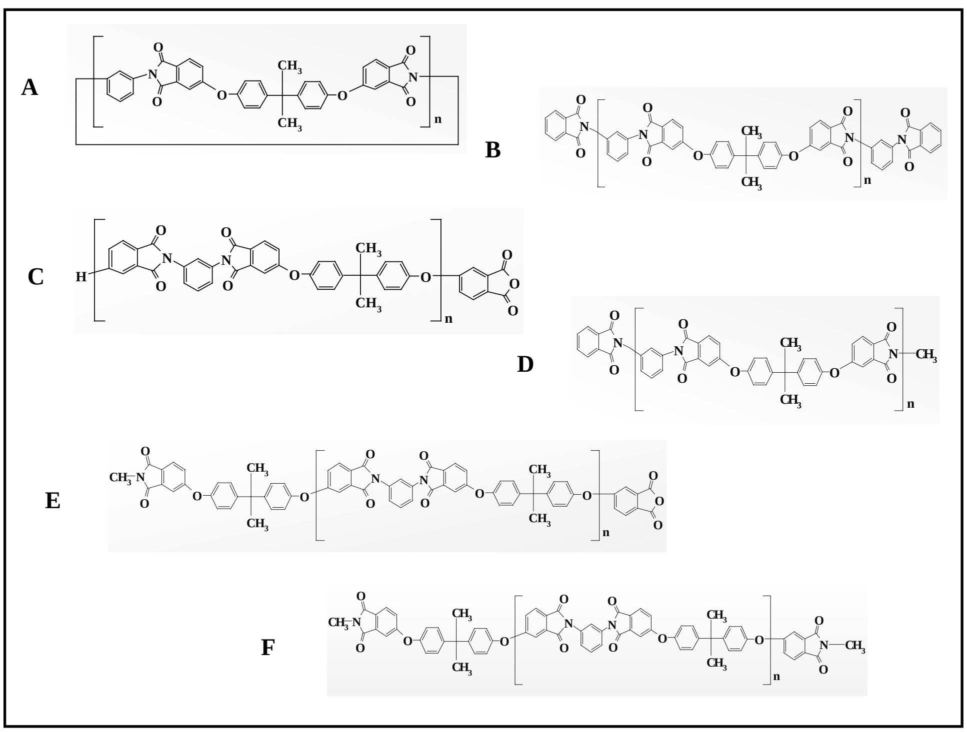
Temperature (°C)	Exposure Time (h)	Mw [a]	Mn [a]	D
	0	14285	11747	1.4
60	144	13700	9377	1.5
	216	12418	8166	1.4
	394	12150	7455	1.6
	594	11577	7085	1.6
	648	11215	6981	1.6
	888	10575	5490	1.7
	1032	8759	4502	1.9

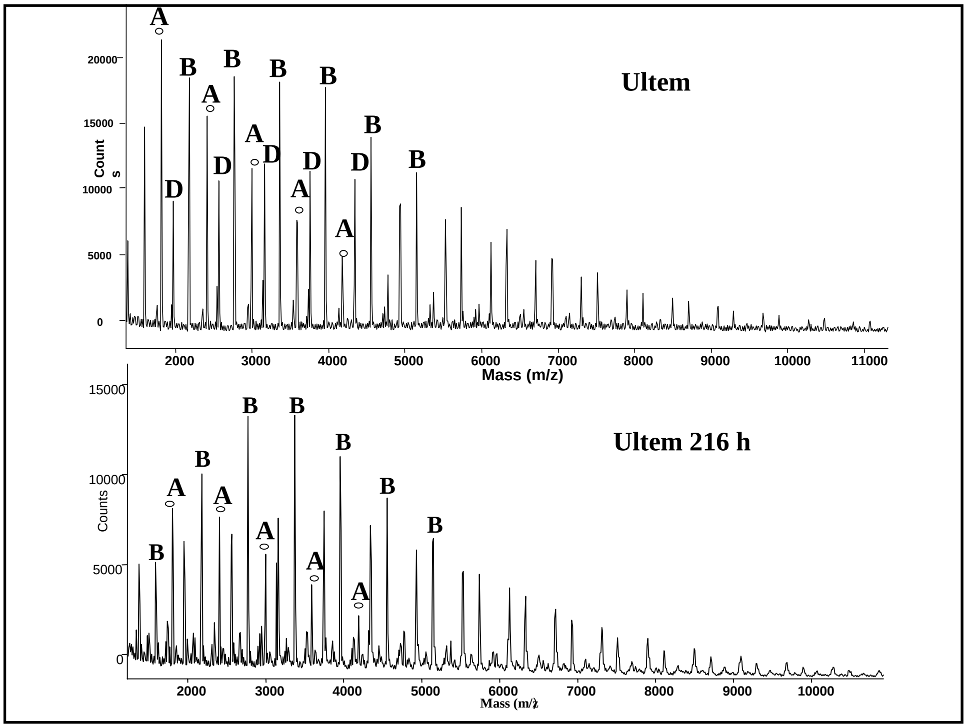
[a] obtained by SEC/MALDI method

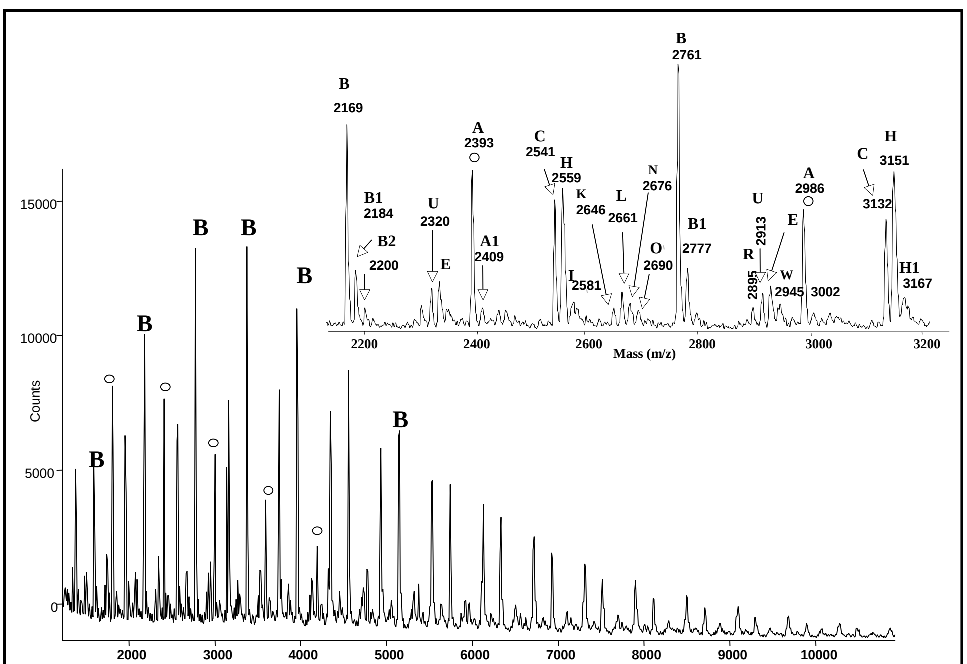


MALDI –TOF Mass Spectra of ULTEM sample

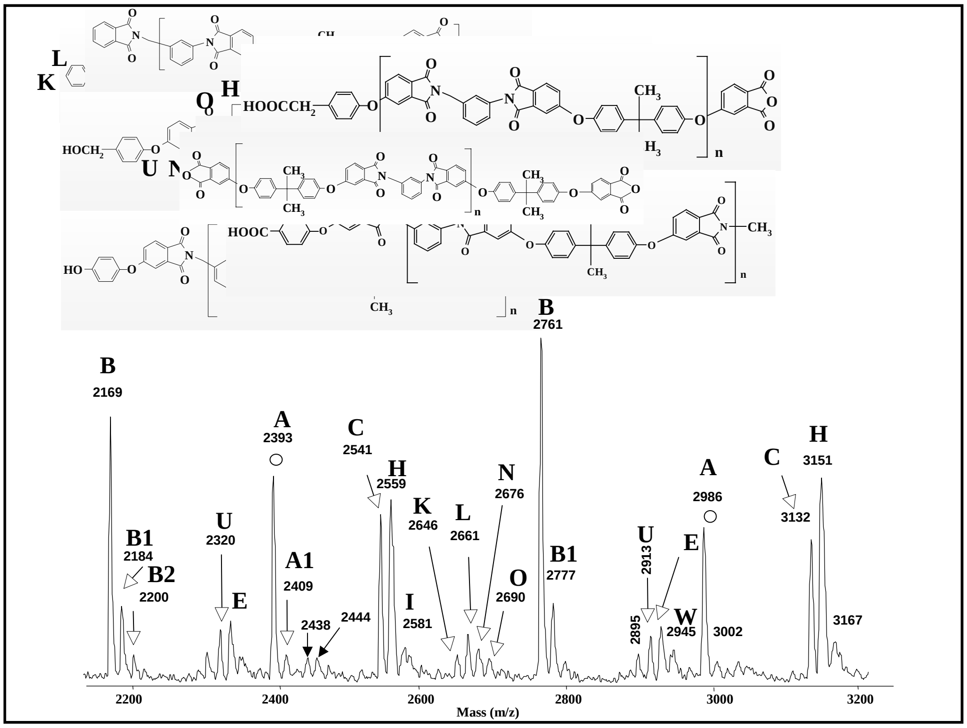

C
F
E
B
2169
A
2393
2761
D
2554
A
2986
D
3147
C
2541
F
2939
C
3132
E
2926
2200
2400
2600
2800
3000
3200
Mass (m/z)

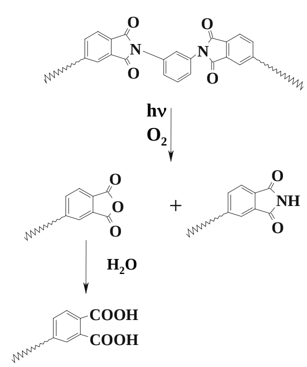

A
B
C
D
E
F



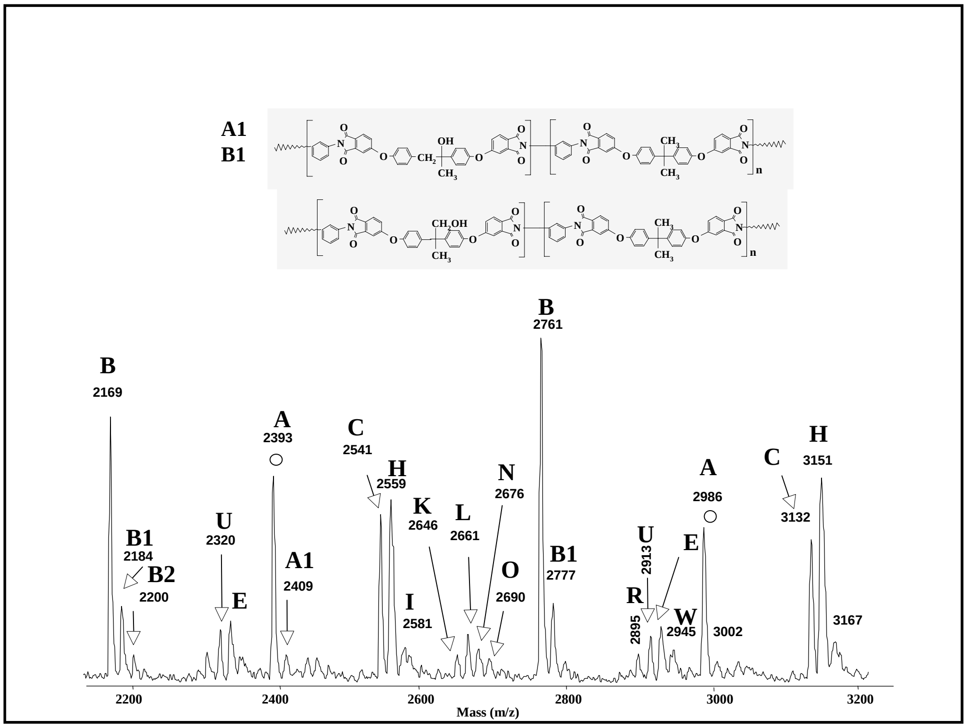


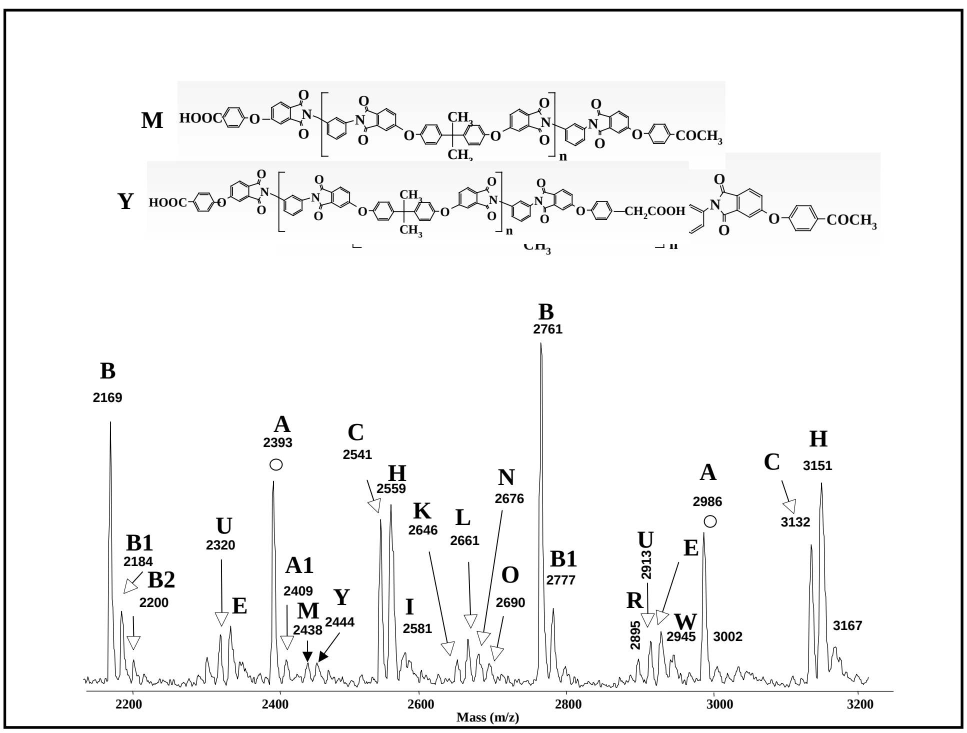
MALDI-TOF Mass Spectra of ULTEM Sample Photo-oxidised at 60°C for 216 hours





Scheme 2:Photo-degradation processes occuring in N-phenilphtal-imide reported by Hoyle et al. *Polymer 1992*


A1
B1
B
2761
B
2169
A
2393
C
2541
H
2559
K
2646
L
2661
N
2676
O
2690
I
2581
U
2320
E
B1
2184
B2
2200
A1
2409
B1
2777
A
2986
C
3132
H
3151
3167
U
2913
E
R
2895
W
2945
3002
2200
2400
2600
2800
3000
3200
Mass (m/z)


M
Y
HOOC
COCH$_3$
CH$_2$COOH
B
2761
B
2169
A
2393
C
2541
H
2559
K
2646
L
2661
N
2676
O
2690
I
2581
U
2320
E
B1
2184
B2
2200
A1
2409
M
2438
Y
2444
B1
2777
A
2986
C
3132
H
3151
3167
U
2913
E
R
2895
W
2945
3002
2200
2400
2600
2800
3000
3200
Mass (m/z)

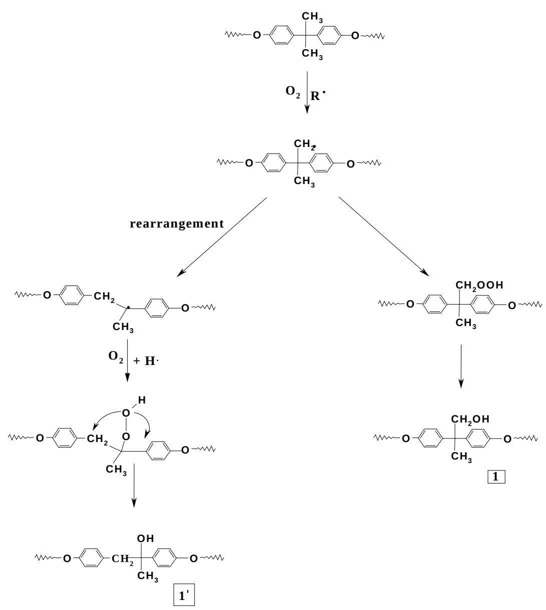


Photo-degradation mechanisms of Bisphenol-A- moiety

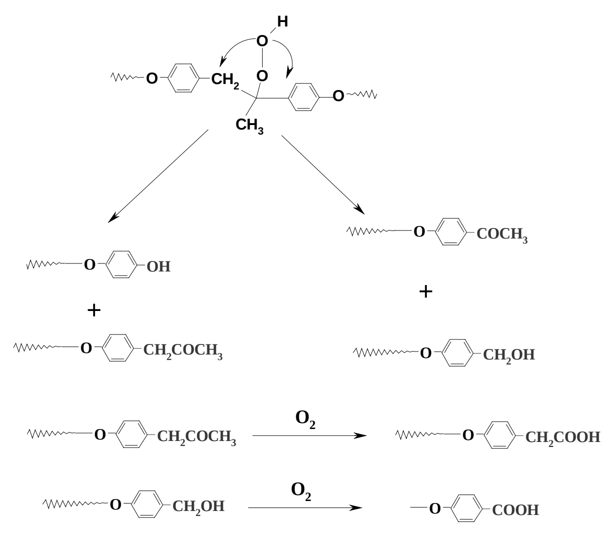
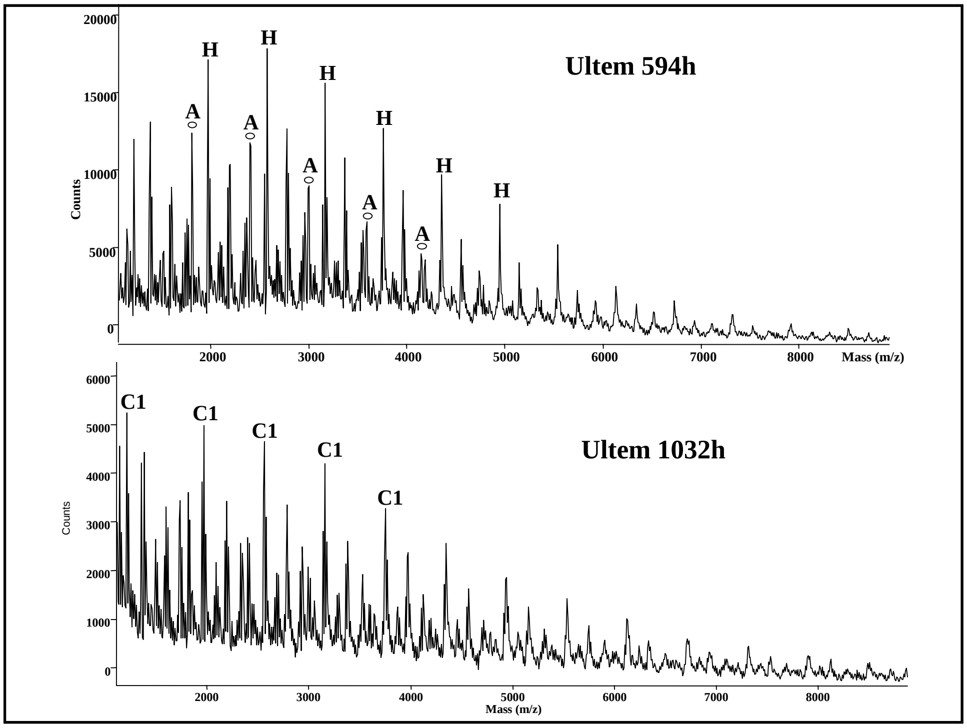
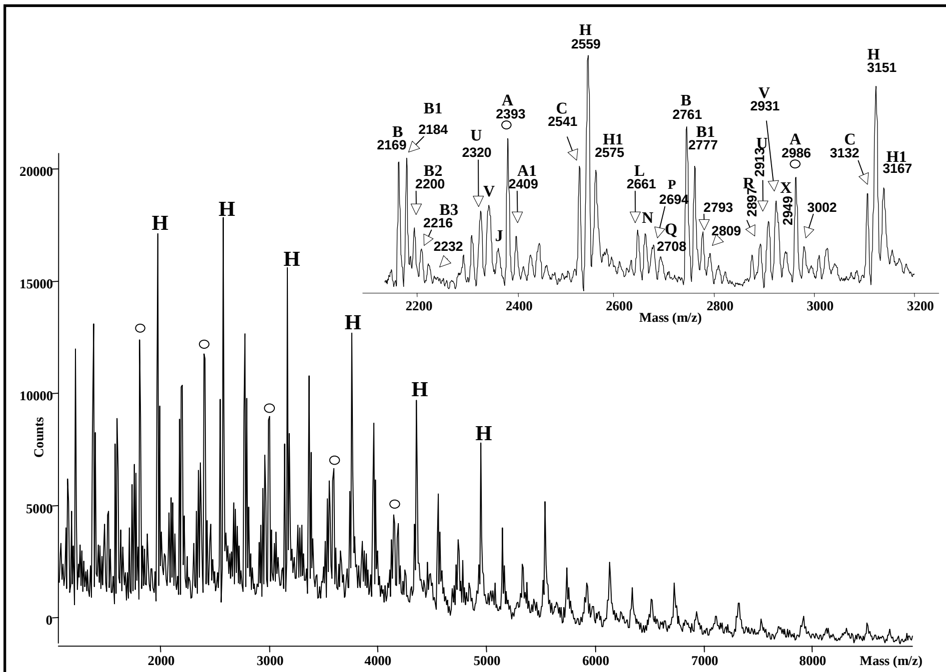
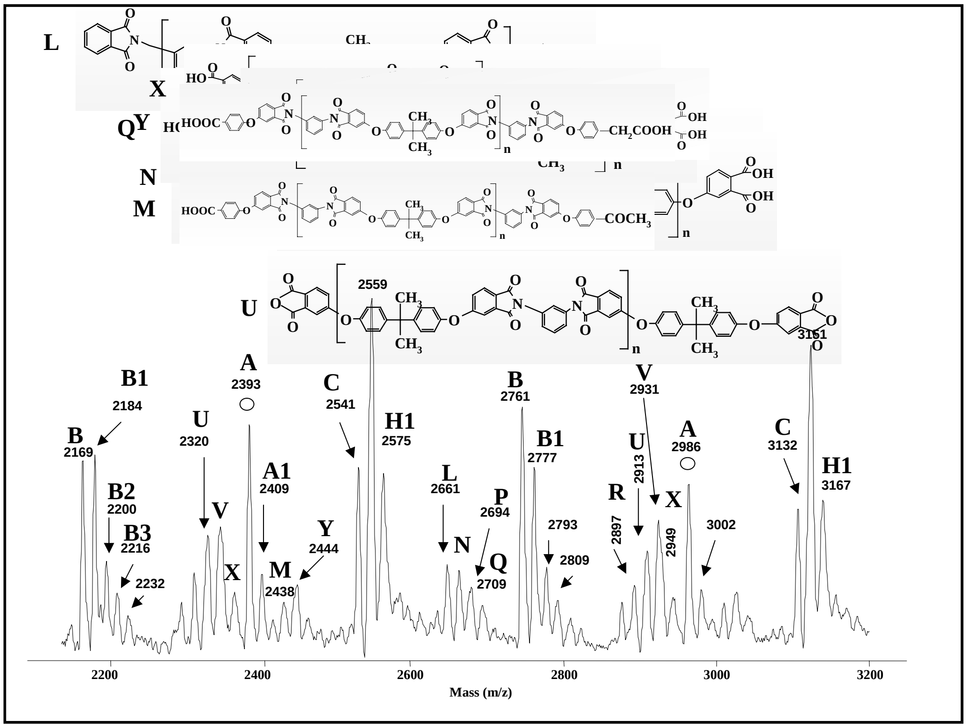


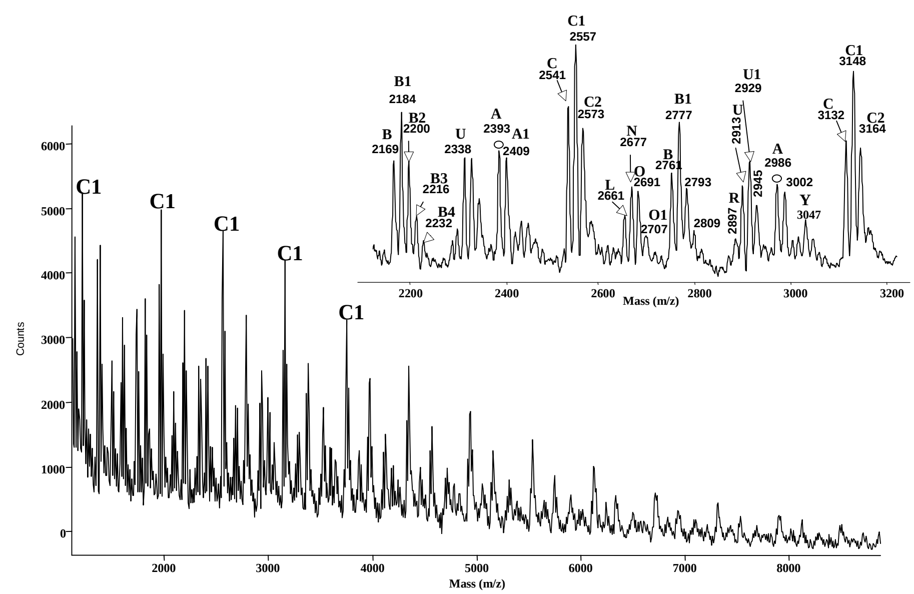
Photo-degradation mechanisms of Bisphenol-A- moiety



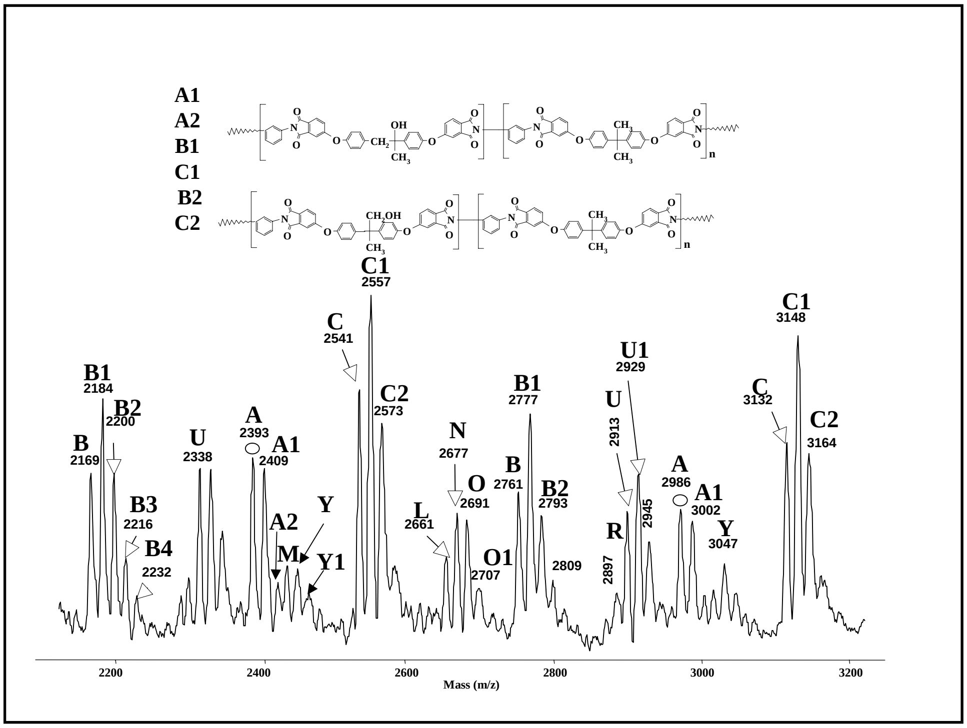


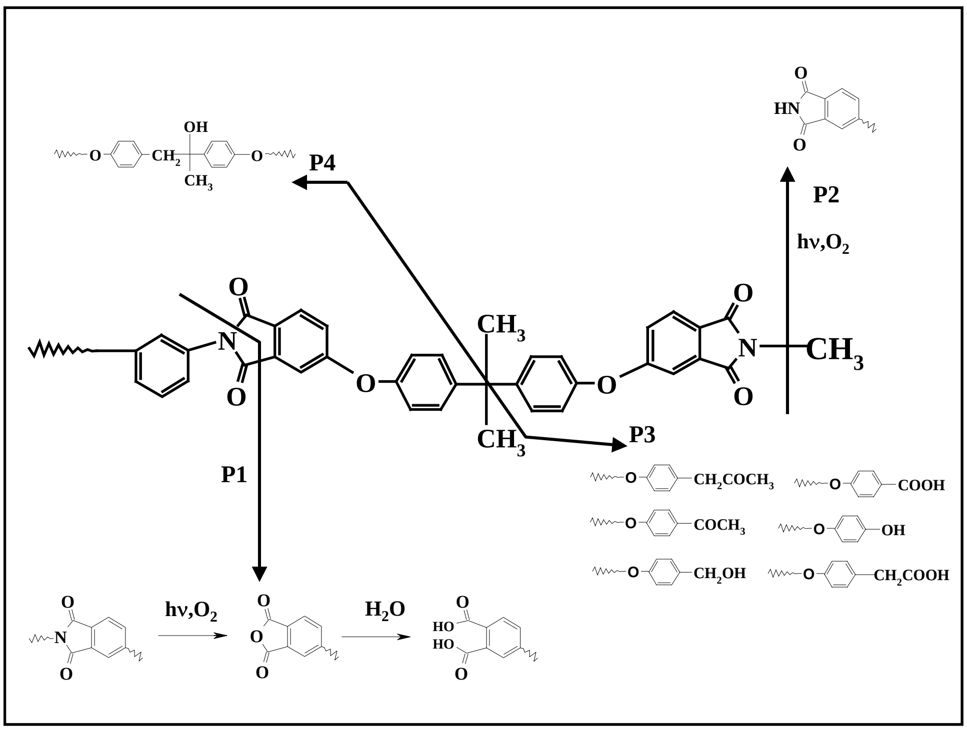
MALDI-TOF Mass Spectra of Ultem sample photo-oxidised at 60 ^{0}C for **594h**





MALDI-TOF Mass Spectra of Ultem sample photo-oxidised at 60 ^{0}C for **1032 h.**


A1
A2
B1
C1
B2
C2
C1 2557
C 2541
C2 2573
B1 2184
B2 2200
B 2169
B3 2216
B4 2232
U 2338
A 2393
A1 2409
A2
M
Y
Y1
L 2661
N 2677
O 2691
O1 2707
B 2761
B1 2777
B2 2793
2809
R 2897
U 2913
U1 2929
2945
A 2986
A1 3002
Y 3047
C 3132
C1 3148
C2 3164
2200
2400
2600
2800
3000
3200
Mass (m/z)


P1
P2
P3
P4
hν,O2
H2O
CH2COCH3
COOH
COCH3
OH
CH2OH
CH2COOH