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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Wiley, Richard H. and Cook Jr., J. Carter(1976) 'Field Desorption Mass Spectral Data for Oligomers up to 2400 Amu', *Journal of Macromolecular Science, Part A*, 10: 5, 811 – 814

To link to this Article: DOI: 10.1080/00222337608061219

URL: <http://dx.doi.org/10.1080/00222337608061219>

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Field Desorption Mass Spectral Data for Oligomers up to 2400 Amu

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ABSTRACT

Field desorption mass spectra of oligomers show peaks of mass up to 2400 amu.

We wish to report the observation of field desorption mass spectra (FDMS) showing ions of mass up to 2400 amu. These were seen in spectra of oligomers and polymers of pivalolactone [1], caprolactam [2], caprolactone [3], and isopropylidenediphenyl carbonate [4], whose EI mass spectra have been recorded previously. The highest

mass peaks were seen in the polypivalolactone spectra.* These data establish new upper limits for the FDMS technique and provide new standards for mass marking in the 1000-2500 amu range.

The polypivalolactone was separated from carefully purified, spontaneously polymerized (presumably with water initiation) monomer. The semisolid polymer, unfractionated and probably containing mostly low molecular weight material, was partially dissolved in tetrahydrofuran or dimethyl sulfoxide with gentle warming and placed on the emitter wire by dipping the wire in the solution. The spectra were recorded by using a Varian 731 mass spectrometer with EI-FI-FD source in the FD mode at 8, 6, and 4 kV accelerating voltages and at 10-22 ma emitter wire current. The spectra, which in the EI mode show a repeating pattern of peaks at approximately $1 + n \cdot 100$, $42 + n \cdot 100$, and $70 + n \cdot 100$ (n is the number of monomer units of 100 amu) up to $n = 11$ (or perhaps higher [1]), show a somewhat simpler spectral pattern in the FD experiments. There is a series of peaks at $19 + n \cdot 100$ and $41 + n \cdot 100$ up to $n = 24$. The water-terminated oligomers correspond to $18 + n \cdot 100$ protonated on the emitter to give $19 + n \cdot 100$ with the next lower $41 + (n - 1) \cdot 100$ fragment being formed by loss of carboxy (45), hydroxy (17), and methyl (15) (total 77). In the range above 2000 amu the intensity of the peaks drops to about one-third that observed in the lower range, presumably because of lower concentrations or decreased volatility of the higher mass oligomers. The mass assignments above 1000 amu were made by linear extrapolation and are of uncertain accuracy. It is noted that at $n = 24$ the accumulated positive mass defect for hydrogen adds up to about 1.5 amu. The theoretical mass values are given in Table 1.

The spectra of the caprolactam and caprolactone oligomers were obtained similarly by using dimethyl sulfoxide suspensions. (The caprolactam samples were supplied by Drs. G. D. Dege and E. M. Pierce of Allied Chemical Co. The caprolactone sample was supplied by Dr. G. L. Brode of Union Carbide Corp.) The caprolactam oligomers were an unfractionated mixture. Their spectra show two sets of peaks corresponding approximately to n monomer units (113 amu) plus 1 to 3 amu up to $n = 16$ (1810 amu) and plus 19 to 22 amu up to $n = 16$ (1830) with uncalibrated peaks at $n = 17-19$. In the lower range these peaks correspond to the protonated cyclic and open chain, water

*Additional data have been obtained using a Varian MAT CH5-DF mass spectrometer. These data confirm the previous mass assignments and extend the range covered to, and perhaps beyond, the 1172 amu peak. The authors thank Mr. J. Wrona for assistance with these measurements.

TABLE 1. Mass Values for Oligomers of Polypivalolactone

$(C_5 H_8 O_2)_x + H_3 O^+$	$(C_5 H_8 O_2)_x + C_3 H_6$
942.518772	1019.542637
1042.571197	1119.595062
1142.623622	1219.647487
1242.676047	1319.699912
1342.728472	1419.752337
1442.780897	1519.804762
1542.833322	1619.857187
1642.885747	1719.909612
1742.938172	1819.962037
1842.990597	1920.014462
1943.043022	2020.066887
2043.095447	2120.119312
2143.147872	2220.171737
2243.200297	2320.224162
2343.252722	2420.276587
2443.305147	2520.329012
2543.357572	2620.381437
2643.409997	2720.433862
2743.462422	2820.486287
2843.514847	2920.538712
2943.567280	3020.591137
3043.619697	3120.643562
3143.672122	3220.695988
3243.724547	3320.748413
3343.776973	3420.800838
3443.829397	3520.853262
3543.881822	3620.905687

(continued)

TABLE 1 (continued)

$(C_5H_8O_2)_X + H_3O^+$	$(C_5H_8O_2)_X + C_3H_6$
3643.934247	3720.958112
3743.986672	3821.010538
3844.039098	3921.062963
3944.091522	4021.115387
4044.143947	
4144.196372	

terminated oligomers. In the higher range the positive hydrogen mass defect must be added. The caprolactone oligomers show peaks differing by 114 amu from approximately 448 amu ($3n + 106$) to 1704 amu ($14n + 106$ to 108) with uncalibrated peaks at similar intervals to the $n = 21$ level. The additional 106 amu are attributed to diethylene glycol (used as "initiator") termination.

The cyclic tetramer of 4,4'-isopropylidenediphenyl carbonate, whose EIMS has been previously reported [4], was also scanned. (The isopropylidenediphenyl carbonate sample was supplied by Dr. A. Factor of General Electric Co.) The FD spectrum shows the molecular ion at 1016 amu, a demethylated fragment at 1001 amu, and an accompanying lesser amount of trimer (762 amu) and dimer (508 amu). The latter are probably present as trace components in the tetramer sample.

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Accepted by editor May 16, 1975

Received for publication September 16, 1975