Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Mass Spectral Characteristics of Pivalolactone and Polypivalolactone

Richard H. Wiley[a]
[a] Hunter College of the Oty University of New York, New York, New York

To cite this Article Wiley, Richard H.(1970) 'Mass Spectral Characteristics of Pivalolactone and Polypivalolactone', Journal of Macromolecular Science, Part A, 4: 8, 1797 — 1818
To link to this Article: DOI: 10.1080/00222337008059522
URL: http://dx.doi.org/10.1080/00222337008059522

J. MACROMOL. SCI.–CHEM., A4(8), pp. 1797-1818, December, 1970

Mass Spectral Characteristics of Pivalolactone and Polypivalolactone

RICHARD H. WILEY

Hunter College of the City University of New York
New York, New York 10021

SUMMARY

The mass spectral characteristics of pivalolactone and its polymer have been determined. The monomeric lactone (MW 100) shows no molecular ion peak but does show peaks at 70 and 42 m/e associated with the loss of formaldehyde and then carbon monoxide and at 56 and 41 associated with the loss of isobutene and carbon dioxide. Only weak peaks, corresponding to the presence of traces of oligomers, are observed above m/e 71. The polymer, at volatilization temperatures of 250-350°C, gives fragments of up to 1242 m/e with a pattern recurring over intervals of 100 m/e units. The principal peaks occur at X42, X70, X83, and X01 m/e. Above 301, the X42 and X70 peaks are observable up to X = 12. The X70 fragment is assigned an acylium isobutyrate radical ion structure and the X42 fragment is assigned an isobutyl radical ion structure. The degradation products are accounted for as being formed from volatilized cyclic oligomers.

INTRODUCTION

Because of its highly crystalline character and its availability from formaldehyde and isobutyraldehyde, there has been a continuing interest in polypivalolactone. There are problems associated with its low melt viscosity, however, and it is possible that these can be related in part to the molecular weight distribution and oligomer content of the polymer.

The determination of varying amounts of cyclic and acyclic oligomers in the polymer through mass spectrometric techniques [1, 2] requires a hitherto unavailable understanding of the mass spectrometric characteristics of the polymer. The present study was undertaken to provide information of this type.

EXPERIMENTAL

The mass spectrometer used in these studies was a medium resolution, cycloidal path instrument (Varian M 66) equipped with variable slits. The operating conditions were: electron energy 68-72 eV except for measurements at high mass and in PFA calibrations at 90 eV; ion energy 69-82 eV except for some of the measurements at high mass made at 92-100 eV; inlet temperature 75°C; analyzer temperature 105-150°C; source temperature 210-280°C; pressures from 6×10^{-8} to 6×10^{-6} Torr; and slit widths varying from one-fourth to three-fourths maximum opening. The exact details for specific measurements are given in the legends for the illustrations. The pressure regulation, which determines the constancy of amount of sample, was difficult to control in the high mass measurements but was held within limits giving reasonably reproducible peak heights in most measurements. There were no excessive variations in peak height over time periods well in excess of those required for the scan. The temperature of the solid sample inlet probe can be determined only to about ±10°C in the intermediate temperature ranges and the calibration of the reading is made outside the analyzer. Simultaneous heating and air flow cooling are used to maintain reasonably constant heating schedules and temperatures during the course of a sequence of readings on a sample. The procedure for obtaining the spectra of the polymers (Figs. 3-23) involves gradually raising the temperature of the sample through the temperature range 250-350°C at which the polymer is volatilized and recording the spectra at the indicated intermediate temperatures after the low mass, volatile components having been removed. Since these conditions do not give uniformly reproducible peak intensities, such data were taken from other spectra under carefully equilibrated conditions. The background and resolution of the instrument were monitored routinely to establish that performance was at specification level (4000 resolution) and with no interfering background at levels well below those at which spectra were recorded. Replicate spectra were recorded for several samples of each material to insure reproducibility.

Materials

The monomer used in these studies was kindly furnished by Drs. E. K. Hall, Jr., R. Taylor, and E. E. Magat of the E. I. du Pont de Nemours and Company. The monomer was stored frozen at 0°C in polyethylene containers. Before use it was purified by repeated recrystallization from the liquid, and by decantation from partially melted solid. Thus purified the sample was water clear at the melting point and contained no more than traces of oligomers or polymers, as evidenced by the absence of peaks above 71 m/e.

The polymer was prepared from the purified monomer with benzyltrimethylammonium hydroxide (Bz) (Triton X100) or with tetrabutylammonium hydroxide [3] (TBAH) (in methanol, DPI 7774). The polymer from the latter had an inherent viscosity of 0.3 in trifluoracetic acid and a melting temperature of 260-265°C as determined by differential thermal analysis. A sample of higher viscosity (inherent viscosity 2.0 in TFA) homopolymer free of additives was also kindly supplied by Dr. E. E. Magat of du Pont. Some of the characteristics of this and related polymers have been reported [4]. Aside from a few peaks, presumably associated with the initiator, no difference was noted in the major features of the mass spectra of these polymers. It is to be noted that at the end of the spectral determination there was no carbonaceous residue left in the sample tube and that there was no background left in the analyzer which could not be removed by a moderate bake-out and pump down.

RESULTS

Typical spectra for the monomeric pivalolactone are shown at two sweep rates in Figs. 1 and 2. The principal peaks occur at m/e 27, 39, 41, 42, 56, and 70. Less prominent peaks are associated with these. The lowest mass peak of prominence occurs at m/e 15 (not shown in the illustrations). The metastable broad peak in the m/e 80-90 range is centered at 84 m/e. The bromoform calibration at 79-82 is shown. The relative intensities of the peaks as taken from spectra run at lower sweep rates give reasonably reproducible (±5%) values. Typical values taken from Figs. 1 and 2 and relative to 41 m/e equal to 100 are: m/e 70(65), 56(40), 42(59), 41(100), 39(48), 29(9), 28(37), and 27(27). There is no peak at the molecular ion mass of 100 m/e and no higher mass peaks distinguishable above the background between 70 and 170 m/e except where trace peaks are observed in samples containing a trace of polymer. There is no

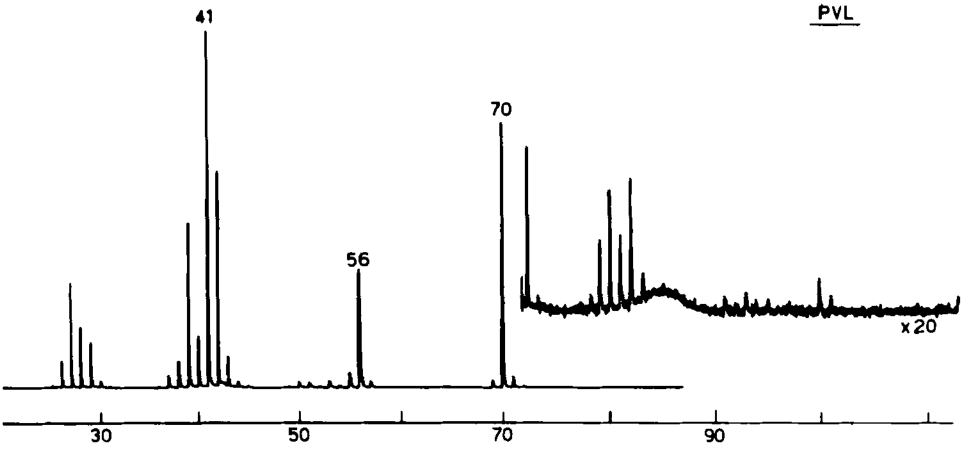


Fig. 1. Mass spectrum of pivalolactone (PVL). Mass range 20-110 amu, pressure 1.2 X 10^{-6} Torr, electron energy 70 eV, ion energy 82 eV, inlet temperature 70°C. Metastable broad peak centered at 84 amu.

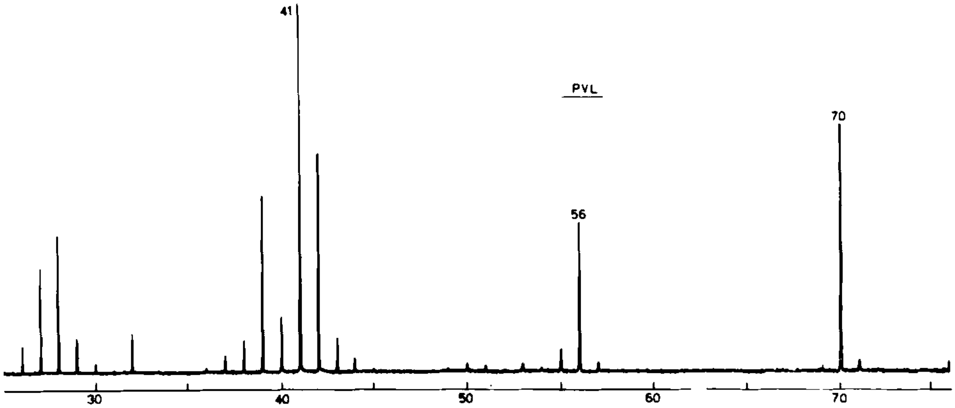


Fig. 2. Mass spectrum of pivalolactone (PVL). Mass range 20-80 amu, pressure 6 X 10^{-8} Torr, electron energy 70 eV, ion energy 82 eV, inlet temperature 75°C. At higher resolution than Fig. 1.

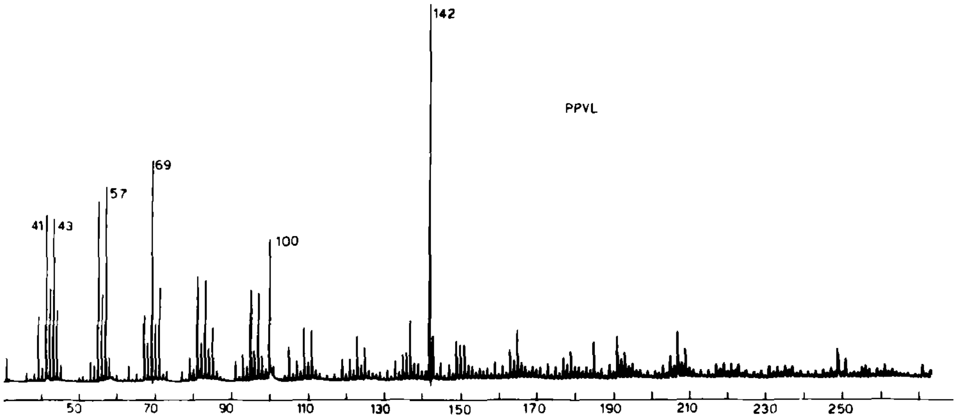


Fig. 3. Mass spectrum of polypivalolactone (PPVL-D) at 220°C. Mass range 20-270 amu, pressure 6 X 10^{-7} Torr, electron energy 68 eV, ion energy 80 eV. Low temperature (lt) spectrum.

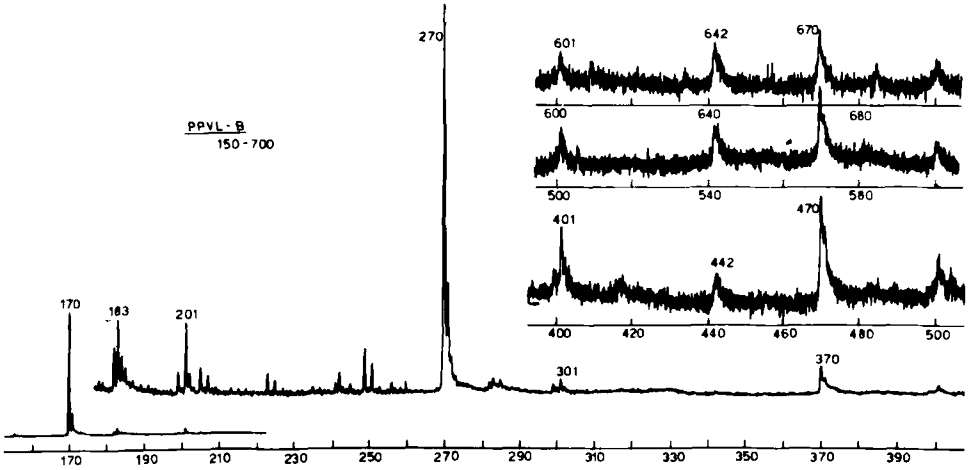


Fig. 4. Mass spectrum of polypivalolactone (PPVL-B) at 290°C. Mass range 150-700 amu, pressure 1-3 X 10^{-6} Torr, electron energy 70 eV, ion energy 92 eV.

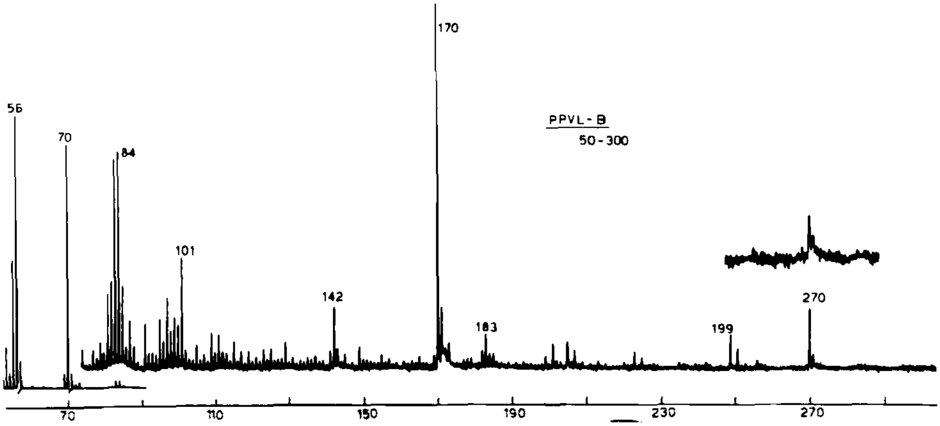


Fig. 5. Mass spectrum of polypivalolactone (PPVL-B) at 340°C. Mass range 50-290 amu, pressure 2.6 X 10^{-6} Torr, electron energy 70 eV, ion energy 79 eV. Metastable broad peak at 84 amu.

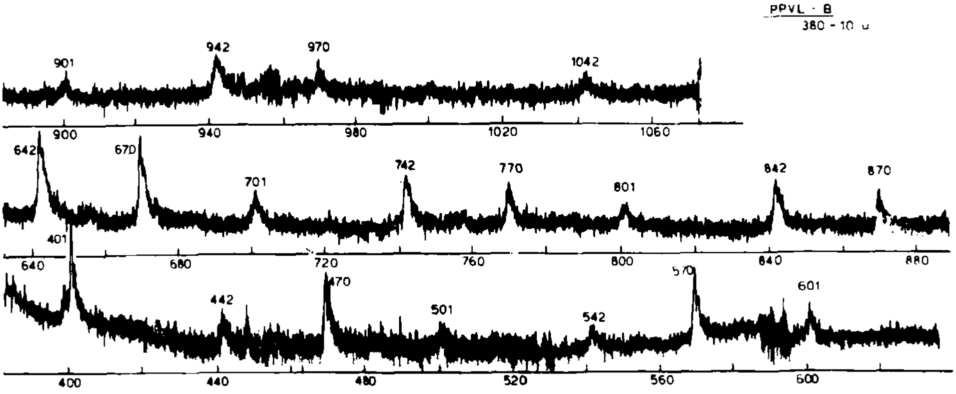


Fig. 6. Mass spectrum of polypivalolactone (PPVL-B) at 280°C. Mass range 380-1070 amu, pressure 4 X 10^{-6} Torr, electron energy 70 eV, ion energy 92 eV. High mass range to 1042 peak.

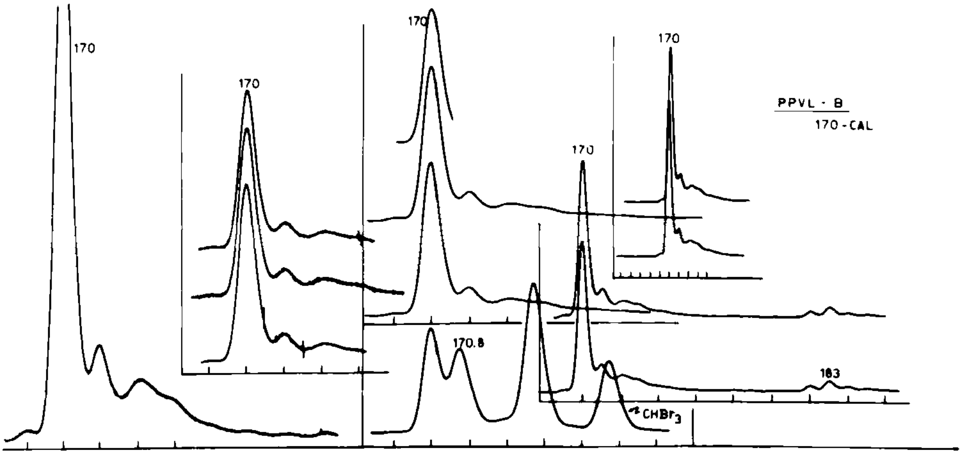


Fig. 7. Mass spectrum of polypivalolactone (PPVL-B) at 280°C. Mass range 169-176 and 168-190 amu, pressure 1.6 X 10^{-7} Torr, electron energy 68 eV, ion energy 84 eV. Calibration with bromoform at 170.05 m/e.

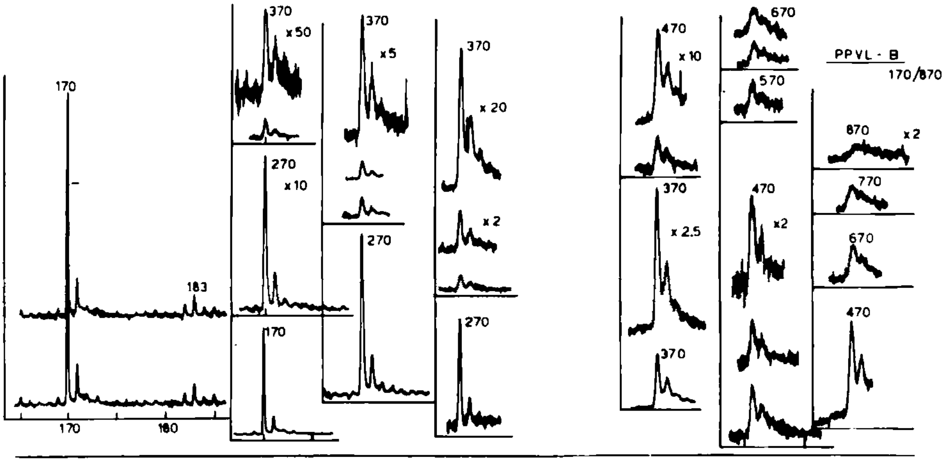


Fig. 8. Mass spectrum of polypivalolactone (PPVL-B) at 340°C. Mass range 165-185 and X70 to 870 amu, pressure 0.6 X 10^{-6} Torr, electron energy 68 eV, ion energy 78 eV. Relative intensities of the peaks at X70.

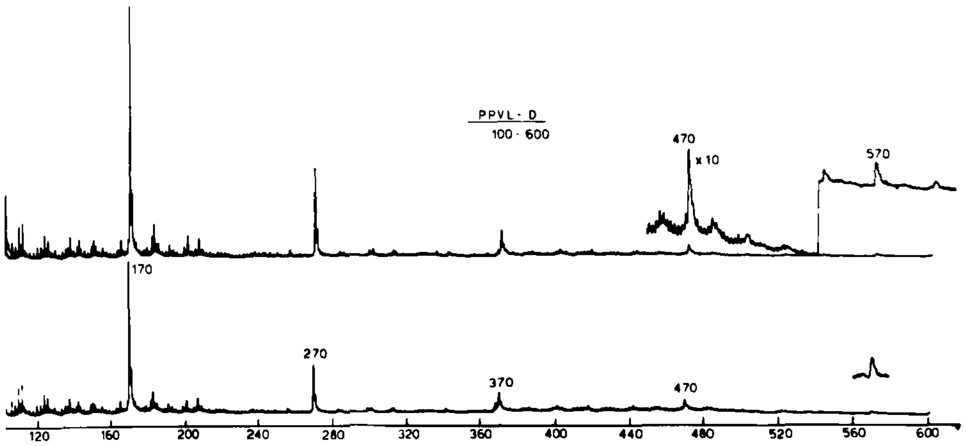


Fig. 9. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 110-600 amu, pressures 3 (lower) and 4 (upper) X 10^{-6} Torr, electron energy 68 eV, ion energy 84 eV. Same range at two pressures.

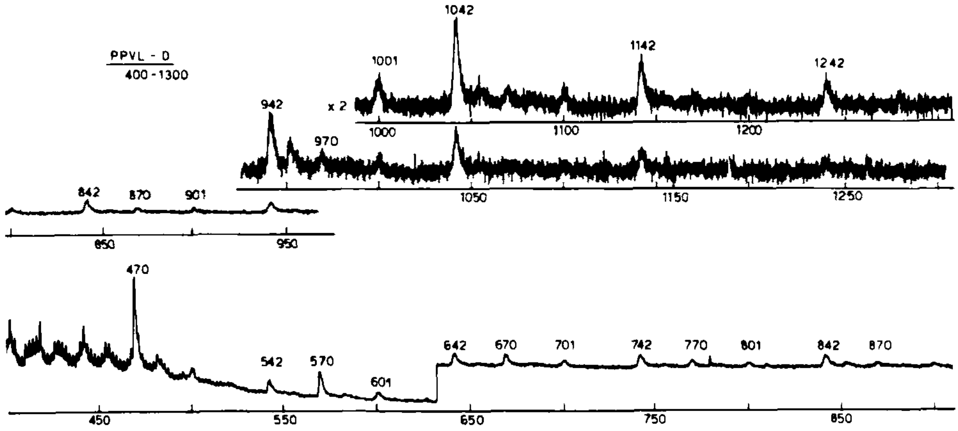


Fig 10. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 400-1300 amu, pressure 3.6 X 10^{-6} Torr, electron energy 68 eV, ion energy 80 eV. High mass range to 1242 m/e.

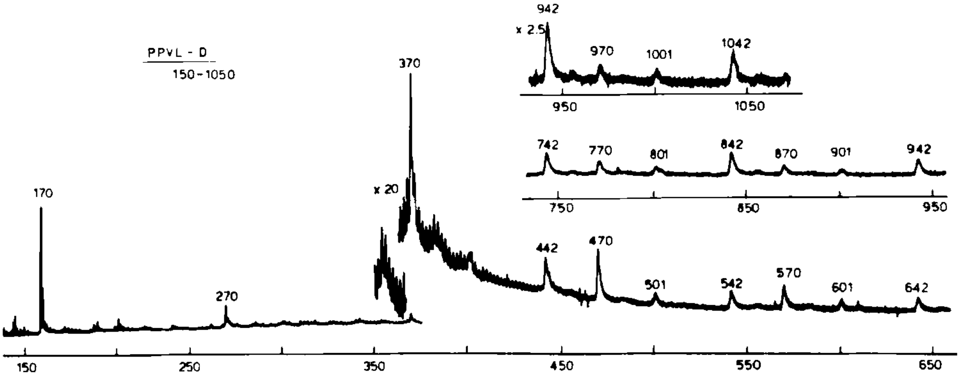


Fig. 11. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 140-650, 740-950, and 940-1050 amu, pressure 5.2 X 10^{-6} Torr, electron energy 68 eV, ion energy 70 eV.

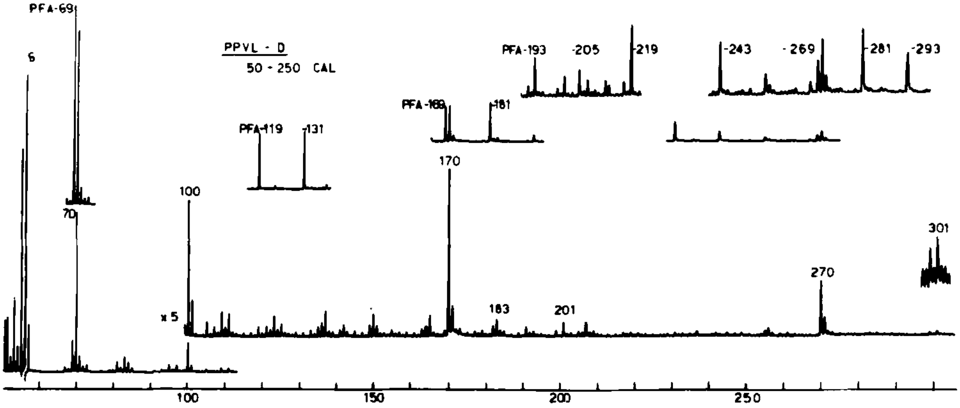


Fig. 12. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 50-300 amu, pressure 4.5 X 10^{-6} Torr, electron energy 68 eV, ion energy 69 eV. Calibration with perfluoroalkane.

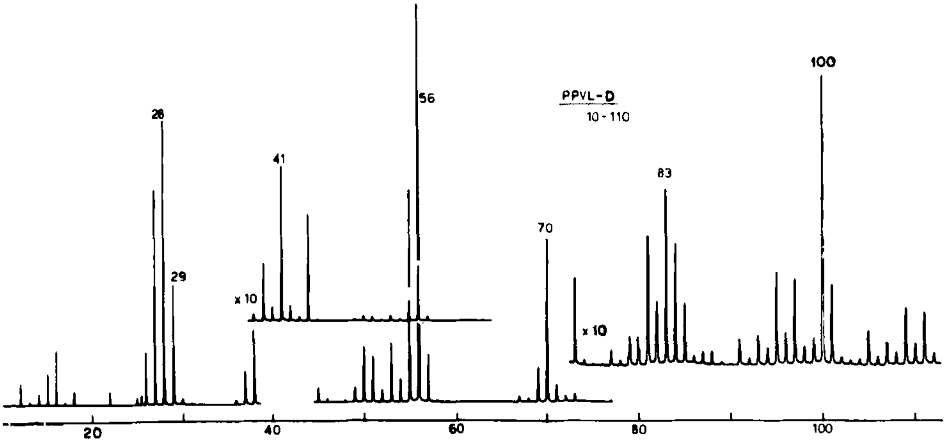


Fig 13. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range at 10-110 amu, pressure 3.6 X 10^{-6} Torr, electron energy 68 eV, ion energy 69 eV. Relative peak heights at slow sweep.

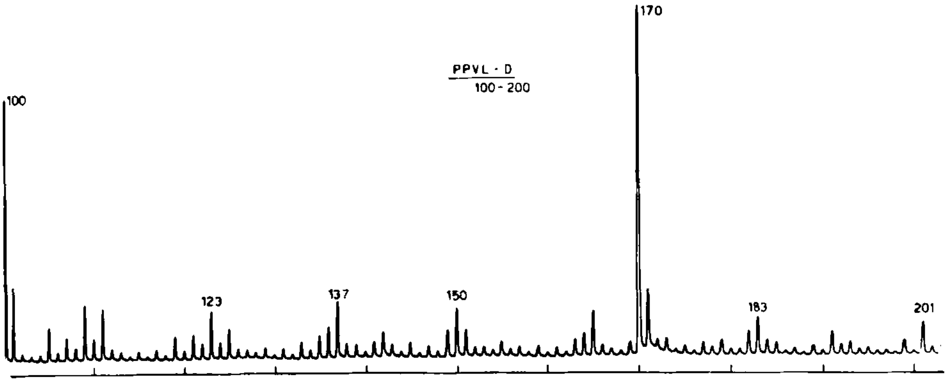


Fig. 14. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 100-200 amu, pressure 3.5 X 10^{-6} Torr, electron energy 68 eV, ion energy 69 eV. Relative peak heights at slow sweep.

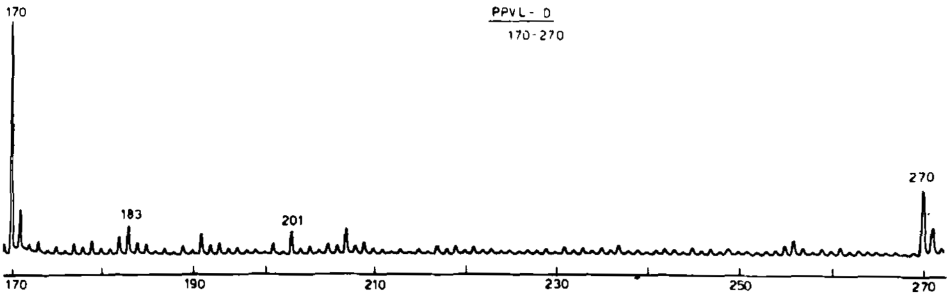


Fig. 15. Mass spectrum of polypivalolactone (PPVL-D) at 280°C. Mass range 170-270 amu, pressure 1.8 X 10^{-6} Torr, electron energy 68 eV, ion energy 72 eV. Relative peak heights at slow sweep.

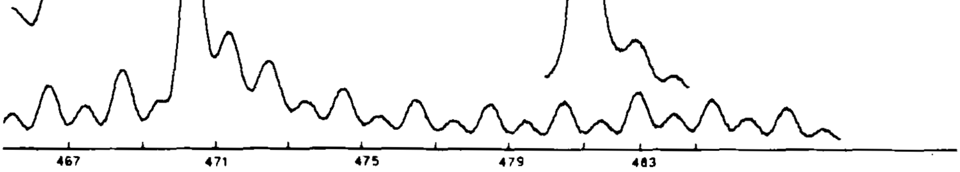


Fig. 16. Mass spectrum of polypivalolactone (PPVL-D) at 290°C. Mass range 465-490 amu, pressure 6 X 10^{-6} Torr, electron energy 69 eV, ion energy 72 eV. Calibration against perfluoralkane at 470.316 m/e. Calculated for $C_{24}H_{39}O_9$ 470.269.

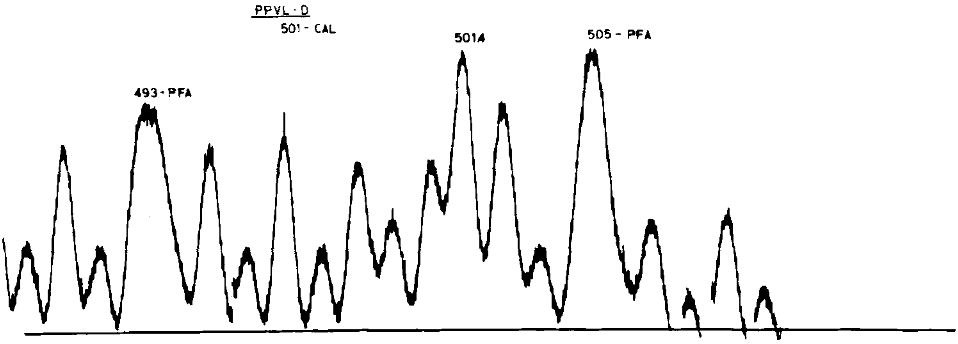


Fig. 17. Mass spectrum of polypivalolactone (PPVL-D) at 290°C. Mass range 490-509 amu, pressure 4.2 X 10^{-6} Torr, electron energy 90 eV, ion energy 82 eV. Calibration against perfluoralkane at 501.4 m/e.

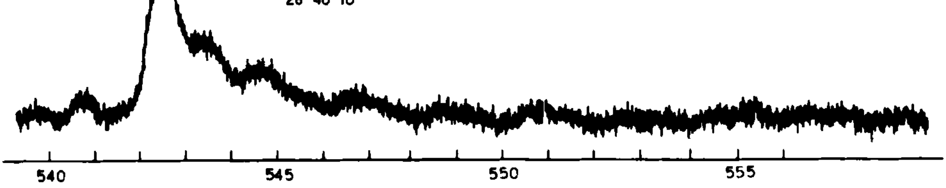


Fig. 18. Mass spectrum of polypivalolactone (PPVL-D) at 285°C. Mass range 540-559 amu, pressure 4.7 X 10^{-6} Torr, electron energy 68 eV, ion energy 82 eV. Calibration against perfluoroalkane at 542.408 m/e. Calculated for $C_{28}H_{46}O_{10}$ 542.317.

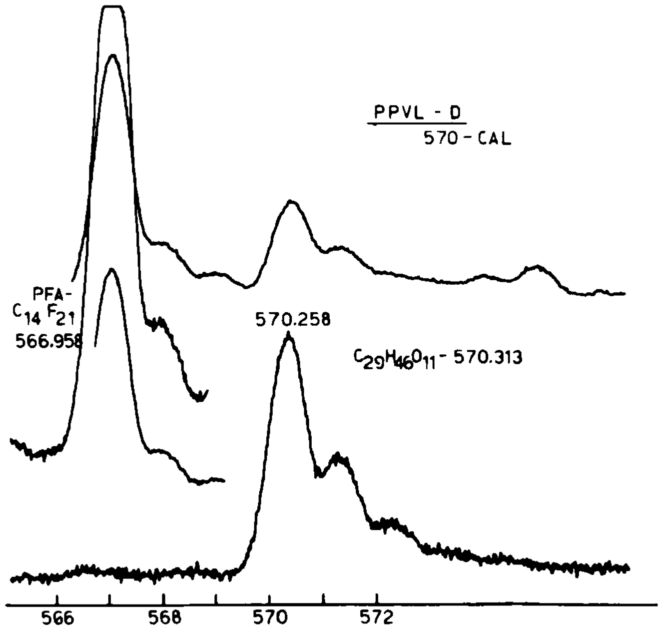


Fig. 19. Mass spectrum of polypivalolactone (PPVL-D) at 290°C. Mass range 565-575 amu, pressure 6 X 10^{-6} Torr, electron energy 69 eV, ion energy 72 eV. Calibration against perfluoralkane at 570.258 m/e. Calculated for $C_{29}H_{46}O_{11}$ 570.313.

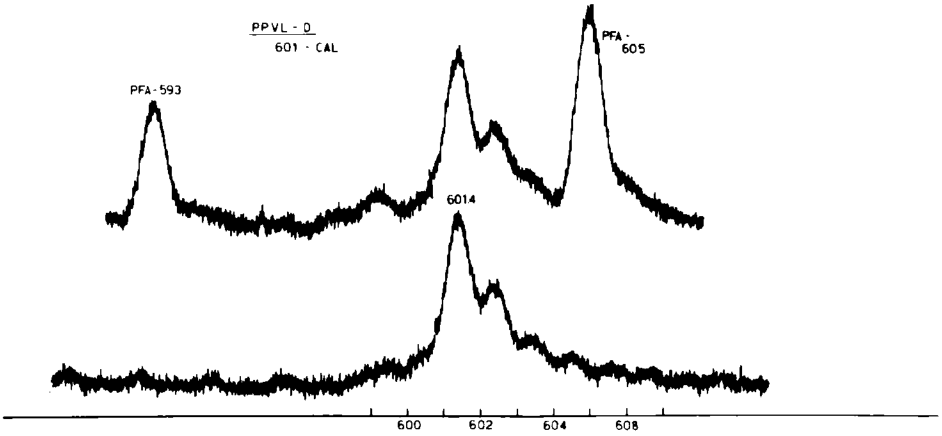


Fig. 20. Mass spectrum of polypivalolactone (PPVL-D) at 295°C. Mass range 590-618 amu, pressure 4 X 10^{-6} Torr, electron energy 90 eV, ion energy 82 eV. Calibration against perfluoralkane at 601.4 m/e.

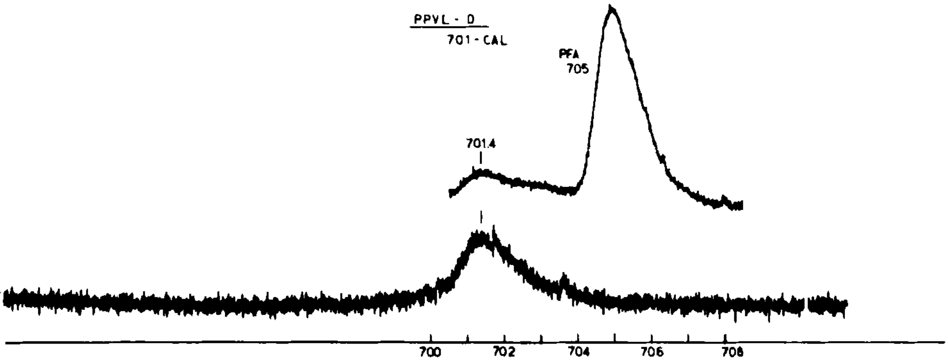


Fig. 21. Mass spectrum of polypivalolactone (PPVL-D) at 290°C. Mass range 700-708 amu, pressure 4 X 10^{-6} Torr, electron energy 90 eV, ion energy 82 eV. Calibration against perfluoralkane at 701.4 m/e.

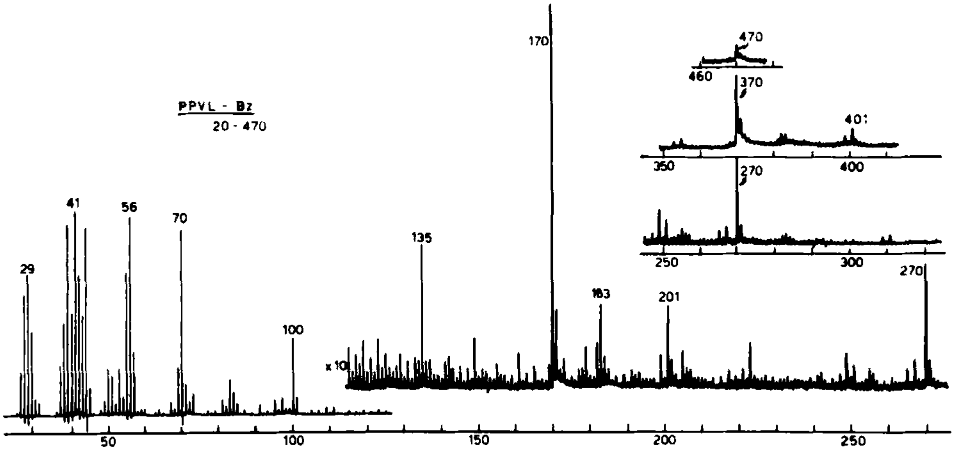


Fig. 22. Mass spectrum of polypivalolactone (PPVL-Bz) at 250°C. Mass range 20-270, 250-320, 350-410, and 460-480, pressure 3 to 8 X 10^{-7} Torr, electron energy 72 eV. Full range spectrum for the benzyltrimethylammonium hydroxide initiated polymer.

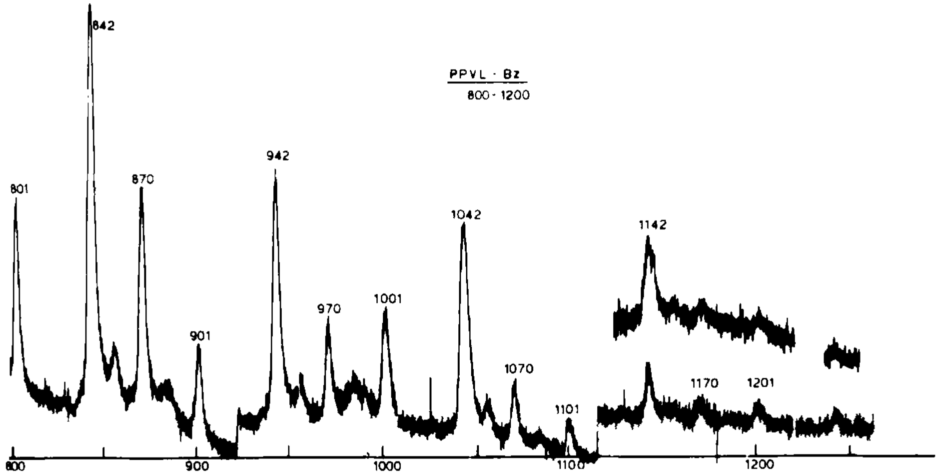


Fig. 23. Mass spectrum of polypivalolactone (PPVL-Bz) at 300°C. Mass range 800-1250 amu, pressure 4 X 10^{-6} Torr, electron energy 90 eV, ion energy 100 eV. High mass range for the benzyltrimethylammonium hydroxide initiated polymer.

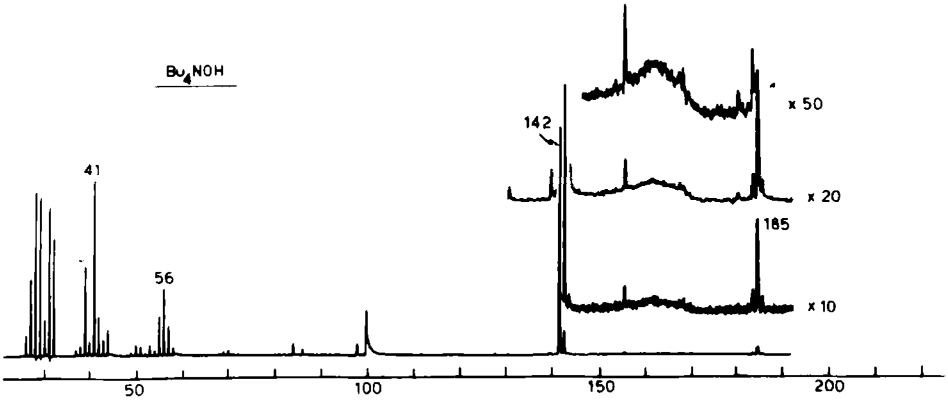


Fig. 24. Mass spectrum of tetra-butylammonium hydroxide in methanol. Mass range 20-200 amu, electron energy 68 eV, ion energy 70 eV, pressure 1.6 X 10^{-7} Torr. Metastable broad peak centered at 163 m/e.

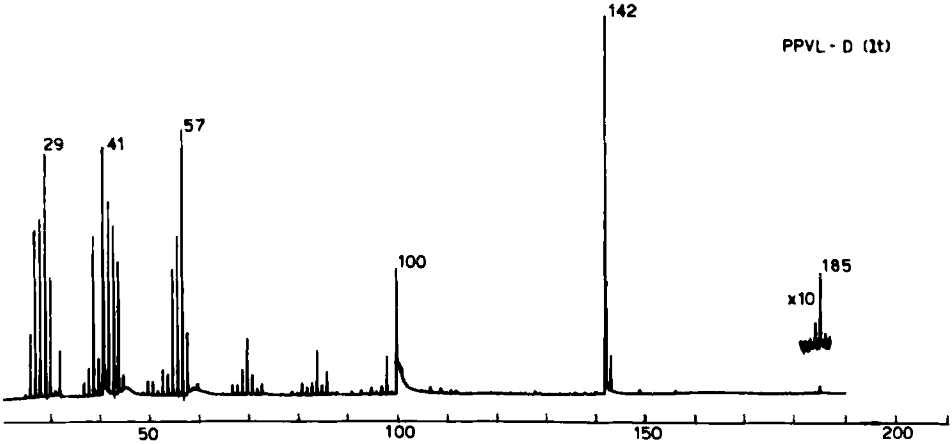


Fig. 25. Mass spectrum of polypivalolactone (PPVL-D) at 180°C. Mass range 20-200 amu, pressure 1.0×10^{-6} Torr, electron energy 68 eV, ion energy 66 eV. Low temperature (lt) spectrum showing 100, 142, and 185 m/e peaks at maximum.

evidence of the prominent m/e 100 and 142 peaks observed for polymer samples at low temperatures; i.e., during initial evacuation (Figs. 3 and 25).

The mass spectra of the polypivalolactone samples are readily obtained on heating the polymer at 250-350°C. This encompasses the temperature (290°C) of onset of degradation of this polymer as determined by TGA measurements. Below this temperature and starting as low as 50-100°C various materials can be volatilized from the sample and these can be related to the history of the sample. These include water, solvents, monomer, and initiator. These can all be removed, and have been, prior to recording the spectra of the polymer, by continued evacuation in the inlet system at temperatures below those at which the spectrum of the polymer is recorded. If this is not done, peaks associated with these components of the polymer sample will be seen in the spectra (e.g., 142 m/e in Figs. 3 and 25). A low temperature spectrum of the du Pont polymer is shown in Fig. 3. Such low temperature spectra do not show the intense peaks at 70 and 170 m/e characteristic of the higher temperature spectra. They do show, in varying intensities and depending on variations in the rate of heating, an intense peak at 142 m/e, an intermediately intense peak at 100 m/e, and a prominent though less intense peak at 185 m/e. The TBAH initiated polymer at low temperature also shows these peaks (100, 142, and 185) as does also TBAH itself (Fig. 24). On further heating (or if heated so rapidly as to have been unobservable) these peaks (100, 142, and 185) decrease markedly in intensity. The 185 peak disappears completely; the 100 peak at first decreases and then increases in intensity but takes a different shape (no daughter ion tailing, Figs. 13 and 24); and the 142 peak is greatly reduced in intensity (Fig. 5), finally disappearing into the background (Fig. 14). Figure 3 is recorded at a time somewhat past the point in this heating schedule when the 100 and 185 peaks are most intense; Fig. 25, at their most intense; Fig. 5, after the 70/170 m/e peaks have appeared. The trimethylbenzylammonium hydroxide initiated polymer shows peaks at 135 m/e (Fig. 22) also presumably derived from the initiator. Figure 25 shows the relation between the 100/142/185 peaks at a lower temperature. The history of the heating schedule at the time of recording a given spectrum will determine the relative intensities of the initiator derived (100, 142, 185) and polymer derived (44, 56, 100, 142, 170, 183) peaks. The initial appearance of the 70 and 170 m/e peaks occurs at a characteristic and reproducible (±10°C) temperature in the 280-320°C range. Below this temperature range the 70/170 peaks are not observed; above, the polymer volatilizes too rapidly to maintain an operable vacuum except when the sample is nearly all consumed. The high mass and metastable broad peaks are seen best at high pressures and with open slit settings.

Representative spectra (at 70 eV) for polypivalolactone samples prepared with TBAH (Figs. 4-8) or with Bz (Figs. 22 and 23) and as supplied by du Pont (Figs. 3, 9-21) are shown in the illustrations. The general pattern, which is shown by all three samples (Figs, 4, 5, 9, 10, and 16) repeats itself in the high mass range over 100 m/e periods up to 1242 m/e (Fig. 10) with sets of peaks at or near the even hundreds (designated X01), at X42, and at X70. The X01 peaks are the weakest over the entire range. It is the 100 m/e peak that is usually observed (Figs. 13, 14 and 22) not the 101 peak (Fig. 5). A peak at 200 m/e has never been observed. The X42 peaks are weaker than the X70 peaks at low masses but over 642 are stronger than the X70 peaks. The set of peaks at X70 are shown in detail in Figs. 7 and 8. Below 100 m/e (Fig. 13) the spectrum is similar to that observed for the monomer (m/e 70, 56, 41, 39) but shows some differences (m/e 83, 44, 25.5). Above m/e 700 (Figs. 6, 10, and 11) the peaks are diffuse and less well resolved, becoming progressively more so as they disappear into the background above 1200 m/e.

Spectra are reproduced in the illustrations to establish the details of the spectral characteristics of the polymer. The high mass range peaks are shown in Figs. 4, 6, 10, 11, 14, and 23. Expanded portions at slow sweep of the spectra for the 10-100, 100-200, and 170-270 ranges are shown in Figs. 13-15. The calibration of the peaks against perfluoralkane or bromoform are shown in Figs. 7 and 12 for the 50-250 range and with more precision in Figs. 16-21 for 471, 501, 542, 570, 601, and 701 m/e. The occurrence of a metastable broad peak in the 80-88 m/e range is shown in Fig. 5. The detail for the X70 range is shown in Figs. 7 and 8. In spectra (not shown) at a resolution 4100 the 28 and 29 m/e peaks are resolved into two peaks separated by 0.350 m/e (C_2H_4-CO, calcd difference 0.0363 m/e).

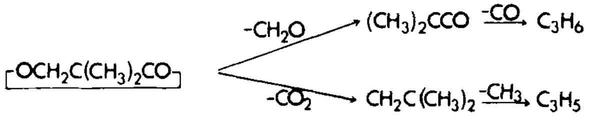
The relative intensities of the peaks, taken from Figs. 13, 14, and 15, show that the abundance of the high mass ions is definitely low. Thus, the relative intensities for the principal peaks are 270(24), 170(93), and 70(430). Above 270 the relative intensities are difficult to assess because of pressure (concentration) variations but the data in Figs. 8-11 give approximate values. From Fig. 11, which is probably the best of those reproduced here for purposes of these comparisons, it can be seen that the X70 peak decreases in intensity by a factor of 2 or 3 for every 100 mass units; the X42 and X01 peaks are insignificant below 200 m/e but above are progressively more intense; and at 742 m/e and above the X42 peak is the most intense. On a scale of 100 for the 170 peak, the low mass peaks (from Figs. 13 and 14) are very intense: 56(1,450), 44(2,800), 41(4,100), 39(1,500), 29(31,000), and 28(75,000).

The spectral characteristics of TBAH, which apparently have not been recorded previously although the spectrum for tributylamine has been [5], are shown in Fig. 24. The base peak occurs at 142 m/e and is accompanied by a broad metastable peak at 155-177 m/e and a daughter at 100 m/e [13]. The highest mass peak is at 185 m/e which corresponds to the tributylamine mass weight.

DISCUSSION

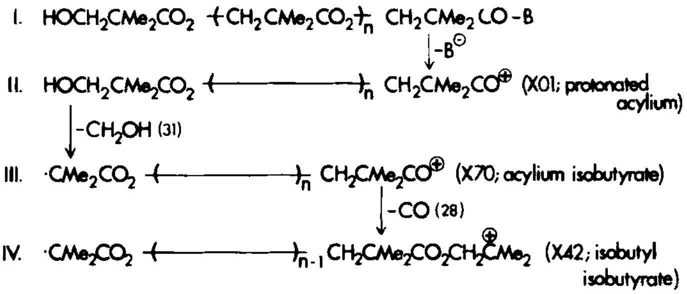
The mass spectrum of polypivalolactone at 280-320°C shows characteristic sets of peaks repeating over ranges of 100 m/e (Figs. 4, 10, 11, and 23). The maxima occur at X42, X70, X83, and X01 up to 1242 m/e. This pattern indicates fragmentation of oligomers, volatilized from the polymer, via processes similar to those observed in the spectrum of the monomeric lactone. The monomer shows maxima at 70, 56, 42, 41, and 39 m/e but none at 100 m/e for the molecular ion (Figs. 1 and 2).

The transformations observed with the monomer are accounted for by two fragmentation pathways: 1) initial loss of formaldehyde (30) to give dimethylketene (70) followed by loss of carbon monoxide (28) to give C_3H_6 (42); or 2) by initial loss of carbon dioxide (44) to give isobutene (56) followed by loss of methyl (15) to give C_3H_5 (41). These transformations are outlined in the accompanying formulas.



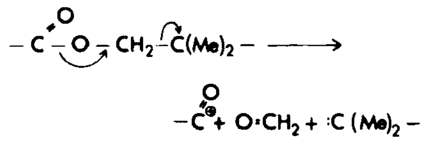
The formaldehyde fragmentation is a reversal of the addition reaction by which the lactone may be formed [6] and has been noted in neopentyl ester mass spectra [7]. The cleavage of β-propiolactone [8] and related structures to give ketenes has been postulated previously to account for mass spectral observations. The carbon dioxide fission has been observed with neopentyl [7] and t-butyl [9] esters, with phenyl pivalate [9], and with lactones [10]. This cleavage is to be correlated with that giving hydrocarbon ions by loss of carbon monoxide from esters [11] and can be expected to be particularly prominently displayed in the spectra from esters of α,α-disubstituted acids since these acid esters can give tertiary carbonium ion structures. The isobutanelike structure thus formed would presumably undergo methyl loss (and migration) such as has been considered previously [12] in analyzing the neopentane degradation pathway. The fragmentation of the ketene structure (m/e 70) involves a metastable transformation as is indicated by the broad peak centered at 84-85 m/e which correlates with the loss of carbon monoxide to give the 42 m/e fragment in accord with the usual factors governing such changes in the cycloidal instrument design [13]. An alternative route starting with the simultaneous loss of two methyl groups from the lactone is less likely as there is no peak at 85 m/e indicative of even partial stepwise loss of the methyl groups.

To account for the major peaks in the spectrum of polypivalolactone, it is assumed that the base terminated structure (I) is ionized as a protonated acylium ion (II) of m/e X01 (X is an integer). The formation of acylium ions in degradations of acids and esters is a generally accepted process. In this particular structure (II), the hydroxymethyl termination would not be expected to be stabile and, consistent with this, the X01 peaks are not intense at low mass. The degradation, as with the monomer, involves loss of protonated formaldehyde (CH_2OH^+) to give an acylium isobutyrate



radical ion (III) of mass X70. The presence of the low intensity X83 peaks in the low mass ranges indicates the loss of methyl plus hydrogen (or CH_4) fragments which was not observed with the monomer. Its occurrence with the polymer is ascribed to the increased probability in the larger molecule, with a higher ratio of methyl to terminal oxymethylene groups, for the methyl cleavage. The acylium isobutyrate structure (III) of X70 m/e then presumably loses, as does the monomer, carbon monoxide to give an isobutyl isobutyrate ion radical (IV) of m/e X42. In order to make these structural assignments as precise as possible, the mass values for the fragments in the 100-300 range (Figs. 7 and 15) and at 470, 501, 542, 570, 601, and 701 (Figs. 16-21) have been made to well less than 1 amu by calibration against perfluoralkane [15].

This fragmentation process can be visualized as taking place stepwise from the ends of an open chain oligomer. Such an acyclic oligomer may be volatilized as such from the polymer but this seems unlikely in view of the ease of decarboxylation of such structures. It is more likely that a cyclic oligomer, a lactone, is the volatilized fragment undergoing degradation. There is precedent [14] for the high vacuum depolymerization of linear polyesters to give cyclic oligomers of low DP. The clean characteristics of the sample volatilization of the polypivalolactone (there is no carbonaceous residue remaining in the sample tube after the spectral observations) suggests that the volatilized fragments are intact cyclic oligomers (lactones) that do not fragment prior to electron impact. The initial fragmentation of the cyclic oligomer may well be either the loss of formaldehyde to give the X70 fragment or the loss of CO and CH_2O to give the X42 fragment.



The X42 fragment is di-stabilized, both ends being branched structures, and this probably accounts for its relatively increased intensity in the high mass range. These fragmentations are comparable to those outlined for the monomeric lactone and involve similar reactions for which precedents were cited above.

There are differences in the low mass range of the spectra for the three samples of polypivalolactone. Some of these differences can be assigned to the initiator. Thus, the spectrum for the Bz initiated polymer shows a peak at 135 m/e (Fig. 22) which is also observed in the spectrum of the base itself. The spectrum of the TBAH initiated polymer shows peaks at 100, 142, and 185 m/e (Fig. 5) again also appearing in the spectrum of the base (Fig. 24). The spectrum for this base shows no molecular ion peak but does show a metastable transition in a broad peak centered at about 163 m/e corresponding to the loss of a propyl group (43 m/e) from the tertiary amine fragment to give $(C_4H_9)_2N{=}CH_2$ via a process previously observed for tertiary amines [5]. The intense peak at 142 m/e (Fig. 3) may also be related to a tetrabutyl ammonium salt initiator of the type stated [3] to be useful in the preparation of this polymer.

ACKNOWLEDGMENTS

The author wishes to thank Drs. E. K. Hall, Jr., R. Taylor, and E. E. Magat of the E. I. du Pont de Nemours and Company for generously supplying samples of the monomer and polymer.

REFERENCES

[1] R. H. Wiley and L. H. Smithson, Jr., *J. Macromol. Sci.*, **A2**, 589 (1968).
[2] R. H. Wiley, *Trans. N. Y. Acad. Sci.*, In Press.
[3] E. I. du Pont de Nemours and Co., Brit. Patent 1,066,123 (1965).
[4] C. H. Leuch, L. F. Beste, and H. K. Hall, Jr., *J. Phys. Chem.*, **67**, 972 (1963); R. Thiebaut, N. Fischer, Y. Etienne, and J. Coste, *Ind. Plastiques Mod.*, **10(2)**, 1 (1962); H. K. Hall, Jr., Abstracts of the Fourth Biennial Polymer Symposium, Amherst, Mass., 1968.
[5] R. S. Gohlke and F. W. McLafferty, *Anal. Chem.*, **34**, 128 (1962).
[6] F. E. Kung, U.S. Patent 2,356,459 (1941); R. H. Hasek and R. G. Nations, U.S. Patent 3,000,906 (1961).

[7] W. H. McFadden, K. L. Stevens, S. Meyerson, G. L. Karabatsos, and C. E. Orzach, *J. Phys. Chem.*, **69**, 1742 (1965).

[8] F. R. Long and L. Friedman, *J. Amer. Chem. Soc.*, **75**, 2389 (1963); see also S. Meyerson and D. McCollum, *Advan. Anal. Chem.*, **2**, 202 (1963); A. S. Newton and P. O. Strom, *J. Phys. Chem.*, **62**, 24 (1958).

[9] M. Fischer and C. J. Djerassi, *Chem. Ber.*, **99**, 750 (1966).

[10] L. Friedman and F. R. Long, *J. Amer. Chem. Soc.*, **75**, 2832 (1953).

[11] W. Sonneveld, *Rec. Trav. Chim. Pays-Bas*, **84**, 45 (1965).

[12] A. Langer and P. Johnson, *J. Phys. Chem.*, **61**, 891 (1957).

[13] H. Benz and H. W. Brown, *J. Chem. Phys.*, **48**, 4308 (1968).

[14] E. W. Spanagel and W. H. Carothers, *J. Amer. Chem. Soc.*, **58**, 654 (1936).

[15] Note added in proof. The precise mass for the 270 peak is 270.1464. The calculated value for $C_{14}H_{22}O_5$ is 270.1467. The author is indebted to Dr. Fred Abramson, Analytical Instruments Division, E. I. du Pont de Nemours and Co., for this measurement. It was obtained on the CEC Model 492 mass spectrometer.

Accepted by editor April 15, 1970
Received for publication June 3, 1970