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On the Mechanism of Thermal Degradation of Polypivalolactone

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In a recent paper, "Thermal Degradation of Poly(2,2-dialkyl-3-hydroxypropionic acid). Living Depolymerization", Manring, Blume, and Dee[1] report a study of the thermal degradation of this family of polymers. On the basis of a variety of evidence including kinetic and TGA data, they conclude that the degradation proceeds via a stepwise "living" process. Toward the end of their paper[1] they address literature mass spectra.[2-4]

Quoting from them: "It is necessary to address the formation of larger cyclic oligomers observed by direct pyrolysis-mass spectrometry (DP-MS) of poly(2,2-dimethyl-3-hydroxypropionic acid) (polypivalolactone).[2-4] Larger cyclic oligomers appear to account for less than 1% (on the basis of the ion intensities in reported MS data) of the overall degradation products of polypivalolactone. Our experimental setup will not detect larger cyclic oligomers. However, on the basis of the mechanism proposed in Scheme I, we anticipate that both transesterification and formation of larger cyclic oligomers must compete with reverse polymerization. Kinetic parameters for these two competing reactions cannot be determined from our data but it is certain they will have different activation energies and frequency factors than the reverse polymerization process. We believe that under most conditions reverse polymerization will dominate transesterification or cyclic formation."

There is, however, evidence for the formation of cyclic oligomers of polypivalolactone (PPVL), observed at relatively large intensities by direct pyrolysis-CI mass spectrometry.[4]

As a matter of fact, the MS apparatus used by Manring et al.[1] will not detect even the simple lactone (which is a primary thermal degradation product) but only CO_2 and olefin (which are secondary thermal degradation products). Aliphatic lactones are difficult to detect in the MS, since they are not stable under EI conditions and soft ionization methods (namely CI) have to be used to reveal them.[4,5] The EI mass spectrum of PPVL, reported in Figure 4a of ref 4, shows that peaks corresponding to molecular ions of cyclic oligomers are absent in the EI mass spectrum.

On the contrary, intense peaks corresponding to NH_4^+ adducts of the cyclic oligomers are present at m/z 118, 218, 318, and 418, respectively, in the ammonia CI mass spectrum in Figure 4b of ref 4.[6]

On the basis of ion intensities in our reported mass spectrum (Figure 4b of ref 4), we can obtain the abundances relative to the cyclic lactones (monomer, dimer, trimer, tetramer) generated in the pyrolysis of PPVL, and these experimental data are collected in the second column of Table I. From inspection of these data, it can be noticed that they are present in sizable amounts.

Evidence that polypivalolactone degrades to form a distribution of cyclic oligomers cannot be disregarded simply on the basis that larger oligomers account for a low percentage of the volatiles detected. Their presence is highly diagnostic, suggesting that they are primary thermal degradation products generated by an end-biting process.

Table I
Distribution of Cyclic Oligomers Generated in the Thermal Degradation of Polypivalolactone[a]

	MS abundance	
n	obsd[b]	calcd[c]
1	100	100
2	0.3	17.7
3	10.0	6.4
4	1.5	3.1

[a] Pivalolactone (n = 1) arbitrarily assigned the value 100. [b] From MS peak intensities in Figure 4b of ref 4. [c] Calculated according to the J-S distribution ($n^{-2.5}$).

The mechanism of formation of these cyclic species has long been debated, and attention has been focused on the content and distribution of macrocyclic compounds produced during depolymerization reactions.[5,11]

The Jacobson-Stockmayer[12] theory predicts that the cyclization probability is related to the mean separation of the reacting sites, and the equilibrium concentration of each cyclic oligomer is predicted to decrease proportionally to $n^{-2.5}$, where n is the ring size expressed as the number of repeating units present. Thus, one should expect low concentrations of higher oligomers. Oligomer distributions calculated according to the Jacobson-Stockmayer (J-S) theory are reported in the third column of Table I.

It can be noticed that the theoretical values are of the same order of magnitude as the experimental ones for the cyclic trimer and tetramer, but there is a large discrepancy for the cyclic dimer (Table I). However, the J-S theory assumes that all the rings formed are strainless, and this condition is not fulfilled when the formation of small rings is concerned.

In the case of the lactonization of ω-hydroxy acids, the cyclization constants versus ring size were found[8,9] to fall by a factor of 10^{-5} from a maximum for the five-membered ring to a minimum for the nine-membered ring. The cyclization constant was then found to rise slowly to a broad maximum value occurring around the 18-membered ring, where the constant is almost 10^3 times larger than at the minimum.[13,14]

Considering that the cyclic dimer of pivalolactone is an eight-membered ring and that trimer and tetramer are 12- and 16-membered rings, we can find some justification for the discrepancies among experimental and calculated values in Table I. Of course, these data are far from being quantitatively satisfactory, and it cannot be claimed that they exclude the possibility of a competing reverse polymerization mechanism for the thermal degradation of PPVL. However, they support strongly the chain-end-initiated, intramolecular-exchange degradation mechanism, which predicts[4,5] the formation of a distribution of cyclic oligomers according to the J-S statistics.[15]

These results are in general agreement with those obtained for a large number of aliphatic polyesters[4,5,11,13,16-18] and also for other condensation polymers such as polyamides, polycarbonates, and polyurethanes, which yield cyclic oligomers as primary thermal degradation products.[5,7-10]

As a consequence, the claim of Manring, Blume, and Dee[1] that they have demonstrated that the thermal degradation of poly(2,2-dialkyl-3-hydroxypropionic acids) occurs mainly (or exclusively) by a reverse polymerization process appears still unwarranted.

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(6) Polypivalolactone was pyrolyzed directly in the ion source with standard Kratos probes heated from 30 to 400 °C at a heating rate of 10 °C/min. As usual in our work,[7-10] the evolving products were analyzed by repetitive mass scans, almost simultaneously with their formation. In Figure 4 of ref 4 were reported the spectra taken at 400 °C, but our evidence is that the relative intensities of the peaks did not change from 300 to 400 °C. When there are changes in the spectra collected at different temperatures, our practice is to report these spectra and to discuss them.[7-10]

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(15) The data presented by Manring et al.[1] are compatible also with the chain-end-initiated, intramolecular-exchange degradation mechanism that we have proposed. A particularly good example of this fact is the block copolymer experiment to demonstrate the direction of polymer degradation. In fact, data in Figures 5–7 of ref 1 show that when poly(2,2-dialkyl-3-hydroxypropionic acids) are terminated with a carboxylate ion, the thermal degradation starts from this end of the polymer chain.

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Registry No. PPVL (homopolymer), 24969-13-9; PPVL (SRU), 24937-51-7.