Response to "On the Mechanism of Thermal Degradation of Polypivalolactone"

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We recently proposed that poly(2,2-dialkyl-3-hydroxypropionic acids) (I) thermally degrade by reverse polymerization when the carboxylic acid terminus is deprotonated and that living depolymerization occurs under some conditions.[1] These proposals were supported by considerable product and kinetic analysis and were not considered exceptional. Although we did not eliminate the possibility of competing processes, the suggestion of reverse polymerization dominating the thermal degradation of I under any circumstances was a subject of controversy. Recently, Garozzo and Montaudo[2] published a paper that maintained that our claims were unwarranted. They suggested[2] that our paper[1] does not give appropriate consideration to the formation of cyclic oligomers which have been reported by many researchers from the thermal degradation of I.[3–6] This paper compares the experimental conditions used in our previous work to those under which many researchers have seen large amounts of cyclic oligomers formed during thermal degradation of I. The data presented here demonstrate that the conditions reported in ref 1, which lead to thermal reverse polymerization and living depolymerization, produce different product distributions than the conditions previously studied.[3–6] Most importantly, cyclic oligomers (larger than monomers) are not observed.

Although ref 1 is presumed to be relevant to the thermal degradation of poly(2,2-dialkyl-3-hydroxypropionic acids) in general, only the thermal degradations of poly(2-methyl-2-propyl-3-hydroxypropionic acid) and poly(2-methyl-2-ethyl-3-hydroxypropionic acid) were studied. Previous studies on the thermal degradation of poly(2,2-dialkyl-3-hydroxypropionic acids) have concentrated on poly(2,2-dimethyl-3-hydroxypropionic acid) [polypivalolactone].[3–8] Although some differences in thermal degradation arise due to different side-chain alkyl groups,[9] it was anticipated (and is still assumed) that these differences would be minor under the conditions described in ref 1. In general, I studied in ref 1 was analytically characterized to a greater degree (molecular weight, architecture, chemistry of the chain terminus) than the polypivalolactone used in previous studies. Indeed, it is the presence of tetrabutylphosphonium carboxylate chain ends that leads to the low-temperature (200–250 °C) degradation described in ref 1.

Previous studies on the thermal degradation of polypivalolactone demonstrate that uncatalyzed thermal degradation is quite slow below 300 °C. Polypivalolactone is reported to degrade to ~10% mass loss after 25 h at 220 °C,[8] whereas I with tetrabutylphosphonium carboxylate chain ends (DP = 51) degrades to 90% mass loss after 33 min at 200 °C.[1] This result is consistent with the known catalytic effect of added base on the thermal degradation of polypivalolactone.[7]

Because of the concern that ref 1 ignores the presence of cyclic oligomers, ref 2 states that "the claim of Manring, Blume and Dee 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 unwarranted". Indeed, the presence of considerable amounts of cyclic oligomer would be inconsistent with reverse polymerization dominating thermal degradation. However, ref 1 did not claim that reverse polymerization of I occurs under all conditions. Reverse polymerization (and living depolymerization) occurs under the specific conditions outlined in the paper. As such, ref 1 emphasizes (both in the Introduction and Conclusions) that other thermal degradation mechanisms (important above 300 °C) will be addressed in a later publication.[9]

In order to address the concerns raised in ref 2, the thermal degradation of poly(2-methyl-2-propyl-3-hydroxypropionic acid) has been monitored by CI/MS techniques similar to those described previously.[3] Cyclic oligomer is observed in amounts consistent with literature reports[3–6] from degradations of carboxylic acid or ester terminated I (occurring predominantly above 300 °C). However, under conditions for which living depolymerization was demonstrated[1] (tetrabutylphosphonium carboxylate terminated, ~250 °C), we detect *no* (<0.1%) *cyclic oligomer.* This observation further establishes the proposal put forth in ref 1 that I can degrade by reverse, living depolymerization and, furthermore, obviates the concerns expressed in ref 2.

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References and Notes

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Registry No. Poly(2-methyl-2-propyl-3-hydroxypropionic acid) (homopolymer), 136893-09-9; poly(2-methyl-2-propyl-3-hydroxypropionic acid) (SRU), 25265-42-3.