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Retraction of the claim of ring expansion polymerization of isobutylene

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I. Abstract

Some three years ago in a preliminary report from this laboratory we have proposed that the polymerization of isobutylene (IB) by the γ-tolyl-γ-valerolactone/BCl_3 initiating system in CH_3Cl or CH_2Cl_2 diluents at -30°C proceeds in a living manner by an unusual ring expansion mechanism and produces macrocyclic polyisobutylenes (PIBs) [1]. Extensive follow-up research confirmed the living nature of the polymerization, however, has failed to confirm the results of a key preliminary experiment upon which the proposition of macrocyclic polymer structure was based. Thus the results of a comparative hydrolysis/GPC experiment carried out with a relatively low molecular weight ($\bar{M}n$=5,400) PIB at -30°C under a blanket of N_2 which gave a lower apparent molecular weight after hydrolysis than the original sample before hydrolysis, could not be confirmed with higher molecular weight samples, i.e., with $\bar{M}n$=12,000, 17,000 and 30,000. As a consequence we wish to retract our earlier claim in regard to the synthesis of macrocyclic PIBs by certain lactone/BCl_3 initiating systems but maintain that these polymerizations proceed in a living manner and yield asymmetric telechelic PIBs, e.g.,α-chloro-ω-carboxyl-PIBs [2].

II. Introduction

tert-Esters complexed with BCl_3 or other Friedel-Crafts acids were shown to be efficient initiators of living carbocationic polymerizations [3-10] and therefore it was expected that tert-lactones i.e., tert-cyclic esters, would also initiate carbocationic polymerization of vinyl monomers. Lactone/Friedel-Crafts acid complexes as initiators may also have certain preparative advantages: They introduce an acid or ester group (depending on the quenching agent) at the α-terminus of the polymer chain and thereby lead to α,ω-asymmetric telechelic PIBs [2]. In addition, we set out to investigate the possibility of preparing macrocyclic polymers by utilizing the living polymerization of vinyl monomers initiated by lactone/Friedel-Crafts acid complexes.

III. Discussion

1. Model Studies

During the early stages of this research model quenching experiments using lactone/Friedel-Crafts acid complexes were carried out to generate insight concerning the mode of decomposition of living polymers. The fact that the addition of pyridine to lactone/BCl_3 complexes yielded the original lactone was regarded to indicate that pyridine quenching of living polymerizations initiated by lactone/BCI_3 complexes yields macrocyclic PIBs [1]. Mounting evidence, however, regarding the mode of decomposition of living polymers and linear ester/Friedel-Crafts acid model complexes, that is, chlorination of the active centers upon quenching [3,4,9], prompts us to revise our earlier conclusion.

It has been recognized that the lactone/BCl_3 complexes are unsuitable models for living PIBs prepared by the use of lactone/BCl_3 initiating complexes, since in the living polymer the five membered ring structure of the lactone is absent. Thus model experiments (that yielded the original lactones [1]) should not have been used to probe the mechanism of decomposition of the active centers in living polymerizations.

Model experiments using the 2,4,4-trimethyl-2-pentyl 4-phenylbutyrate/BCI_3 complex have shown that quenching by a large variety of nucleophiles invariably yielded a tert-chlorine at the chain end and that a quenching method that would have preserved the ester group could not be developed [2]. Evidently these quenching methods are unsuitable for the preparation of macrocyclic PIBs.

2. PIB characterization

Detailed reexamination of PIBs prepared by the use of the γ-tolyl-γ-valerolactone/BCl_3 initiating complex and pyridine quenching revealed features which indicate the existence of linear polymer structures. Elemental analysis of a $\bar{M}n$=4,500 PIB sample yielded a chlorine chain-end functionality of $\bar{F}n$=1.11. GPC analyses of a series of polymer samples obtained by quenching aliquots of living polymerization systems simultaneously with pyridine or methanol gave theoretical molecular weights within experimental variation (10%), which indicates that both quenching methods yield the same linear structure. In our preliminary paper [1] we reported a shift in the GPC trace toward lower elution volumes (higher molecular weights) upon hydrolysis of an $\bar{M}n$=5,500 polymer. This shift upon hydrolysis was regarded a supporting evidence for the ring structure of the original polymer, however, this result could not be reconfirmed with higher molecular weight samples, i.e., with $\bar{M}n$=12,000, 17,000 and 30,000.

Evidently, the earlier result was an artifact related to conditions during hydrolysis and subsequent sample isolation.

IV. Conclusion

Detailed studies with the 2,4,4-dimethyl-2-pentyl-4-phenylbutyrate/BCl_3 model system, chlorine analyses of low PIB oligomer and hydrolysis experiments with higher molecular weight PIB indicate that contrary to our earlier claim the method described in our earlier paper (1) does not produce and is unsuitable for the synthesis of macrocyclic PIB. On the basis of the results of follow-up investigations and additional studies relative to the structure of PIBs prepared by lactone/BCl_3 initiating systems followed by pyridine quenching, we are compelled to retract our earlier claim in regard to the synthesis of macrocyclic PIBs. According to the results of these latter studies, to be published elsewhere (2), these products are in fact linear α,ω-asymmetric telechelic PIBs.

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