



***Synthetic and Mechanistic Studies of Poly(vinyl chloride) and
Some Other Chlorinated Polymers***

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Abstract

Poly(1,2-dichloroethylene) (PDCE) is an unknown polymer that should be a superb engineering thermoplastic for use in a variety of high-performance applications. This thesis discusses approaches to its synthesis and describes the preparation and some of the properties of a number of new polymers that contain chlorine. Other major topics addressed here are (a) the involvement of an excited cation diradical intermediate in the thermal degradation of poly(vinyl chloride) (PVC) and (b) the mechanism of the thermal stabilization of PVC by "plasticizer thiols". Unlike vinyl chloride, 1,2-dichloroethylene (DCE) undergoes dimerization under free-radical conditions. Chain transfer to DCE by β -Cl elimination was shown to be the major reason for its nonpolymerization. The dimeric radical rearranges by a 1,2-Cl shift, but apparently to only a very minor extent.

During the chlorination of alkyl chlorides with molecular chlorine, a bridged intermediate is involved, and for this reason, vicinal chlorides were found to be the major products. The yields of geminal chlorides increased significantly in the presence of solvents that form complexes with chlorine atoms, but such solvents also decreased the reactivity of the chlorination. Thus the chlorination of PVC in the presence of complexing solvents was not a useful method for the synthesis of PDCE

Polyacetylene (PA) was prepared by the methods of both Shirakawa and Luttinger. The PA's were chlorinated with Cl_2 , and as a result, white polymers were obtained. However, neither of the PA's could be chlorinated completely, in that double bonds were invariably left in the polymer backbone. The chlorinated PA's had a much higher glass transition temperature than PVC but were much less thermally stable, apparently owing to the presence of allylic chloride groups. The molecular microstructure of chlorinated PA remains unclear.

Ring-opening metathesis polymerization (ROMP) followed by addition chlorination with Cl_2 provided an approach to the preparation of a series of new polymers that could be interesting technologically. However, experiments with model compounds showed that the addition chlorination of conjugated double bonds or the double bonds of allylic dichlorides is slow and frequently incomplete. The chlorination of ROMP polymers made from cyclopentadiene, 1,3-cyclooctadiene, and 1,3,5-cyclooctatriene also did not proceed to completion, and there was hardly any chlorination at all of a very interesting $-(\text{CH}=\text{CHCHClCHCl})_n-$ polymer made from *cis*-3,4-dichlorocyclobutene. Thermal degradation of a series of model compounds indicated that polymers containing $(\text{CHCl})_n$ ($n \geq 3$) structures would have low thermal stability.

Polyene sequences formed during the thermal degradation of PVC were found to interact with HCl in order to form an ion pair whose thermal excitation produces a triplet cation diradical. This diradical abstracts a hydrogen atom from a methylene group of PVC, and the ensuing β -Cl scission forms an internal allylic chloride structural defect. As more of these defects are created in the same way, the autoacceleration of thermal dehydrochlorination occurs.

A "Plasticizer thiol", 2-ethylhexyl 3-mercaptobenzoate, was confirmed to be an excellent thermal stabilizer for PVC. Preliminary experiments strongly suggested that its mechanism of stabilization involves both the removal of labile chloride by nucleophilic substitution and the shortening of polyene sequences by addition to double bonds.