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Free-radical chain generation of ketene during the synthesis of liquid crystalline aromatic polyesters

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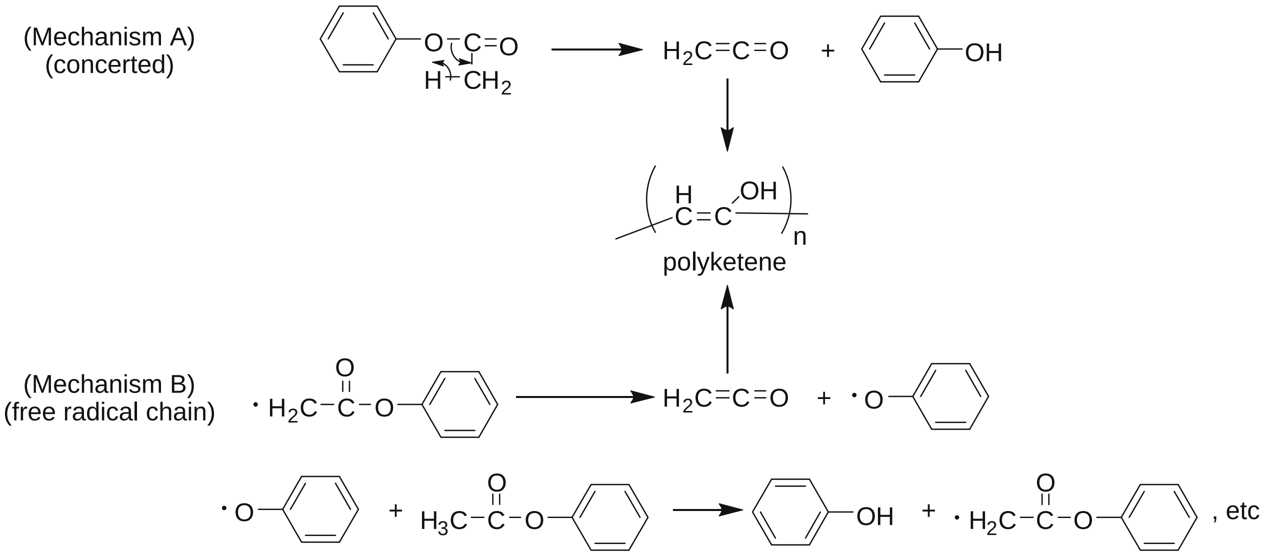
A B S T R A C T

At the high temperatures used for the preparation of liquid crystalline aromatic polyesters (LCPs), ketene cleavage occurred from acetoxyarenes. Ketene is known to oligomerize to colored oligomers which may be responsible for an undesirable yellow color in LCPs. Thermolysis of the model compound *p*-acetoxybenzoate gave ketene oligomers and methyl *p*-hydroxybenzoate, which oligomerized. A free-radical chain reaction mechanism for ketene formation was demonstrated by the reaction of tributyltin hydride with haloacetoxyarenes.

1. Introduction

This study explored the possibility of ketene formation and oligomerization contributing to the yellowing observed during aromatic main chain liquid crystal polymer (LCP) synthesis.[1,2] Such yellowing limits potential LCP uses as optical materials. In earlier LCP work, it was shown that at high polymerization temperature some of the mixed anhydride intermediates thermolyze to ketene and aromatic carboxylic acid; a nitrogen sweep carried ketene out of the reaction to a trap where its occurrence was demonstrated by the reaction with aniline to form acetanilide (**3**).[3] If the ketene is left in the reaction, it can oligomerize; and polyketene is variously described as ranging from yellow[4] to dark brown-black.[5]



Scheme 1.

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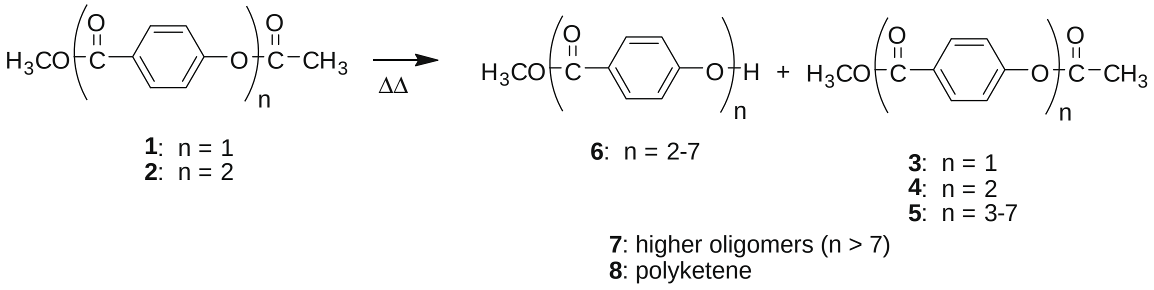
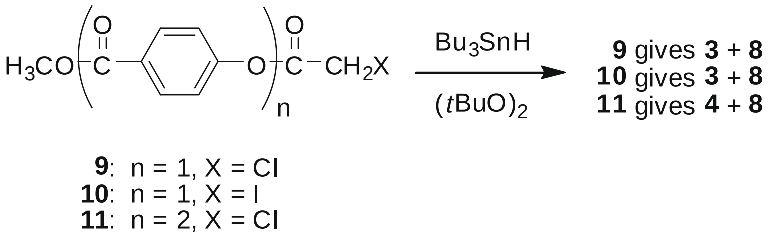


Scheme 2.



Scheme 3.

The mechanistic question arises: Is this ketene formation a concerted electrocyclic reaction (Scheme 1, A) or a free-radical chain reaction (Scheme 1, B). The literature[6–11] supports either mechanism.

2. Reactions in the absence of free-radical generators (Scheme 2)

Heating either model acetoxyarene **1** or **2** at 280–320 °C for 20 min gave a dark yellow reaction mixture. The mixtures were analyzed by GC–MS. Isolation of low molecular weight products was done by flash column chromatography. Higher oligomers were detected using ESI-MS techniques. An intractable residue, soluble only in pentafluorophenol, presumably a mixture of higher molecular weight oligoesters, was also formed. The yellow component of **8** was highly polar, requiring methanol for elution but it could not be more closely characterized. These results are explained by thermal cleavage of **1** or **2** to hydroxyesters **3** and **4** which can undergo intermolecular methanolysis to form **3**–**5**.

3. Reactions in the presence of free-radical generators (Scheme 3)

Hydrogen abstraction was achieved by heating **1** with di-*t*-butyl peroxide at 150 °C under argon gave a mixture of **3** and polar yellow material **8**, along with unreacted **1**. More decisively, halogen abstraction was achieved by heating the halo compounds **9**–**11** with tributyltin hydride in the presence of di-*t*-butyl peroxide which converted them to **3** and **4** in virtually quantitative yields.

4. Conclusions

At high temperature polymerization used in LCP synthesis, model compounds **1** and **2** cleave to ketene and two sets of *p*-oxybenzoyl oligomers. To decide whether the cleavage mechanism was either a concerted or a free-radical chain, the feasibility of the latter mode was demonstrated at lower temperatures. The postulated chain-carrying acyloxy radical was generated by either hydrogen or halogen abstraction and shown to readily lose ketene.

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