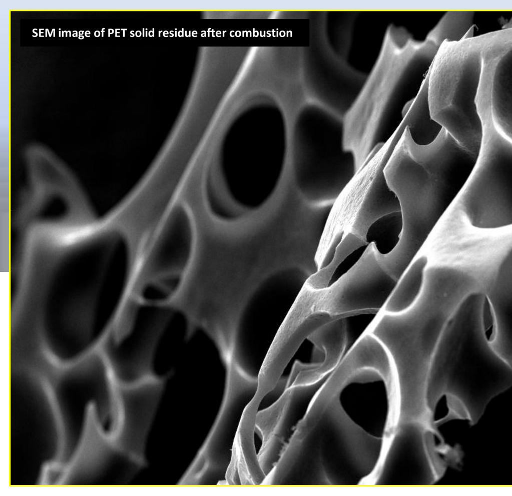
Carbonization Mechanisms of PET

The Chemical Understanding

P. SEBASTIANELLI, J. ALONGI, D. BATTEGAZZORE, G. CAMINO

Politecnico di Torino – Alessandria Site – V. Teresa Michel 5, 15100 Alessandria (Italy)
INSTM and NIPLAB Research Unit
e-mail: paolo.sebastianelli@polito.it ; jenny.alongi@polito.it; daniele.battegazzore@polito.it; giovanni.camino@polito.it



INTRODUCTION

The understanding of charring mechanisms in polymer thermal decomposition is of paramount importance because it may provide a more suitable, environmentally friendly approach to fire retardance of polymer materials. Indeed, charring occurs in competition and at the expenses of formation of volatile combustible products from the polymer exposed to fire conditions.
For what concerns the PET:

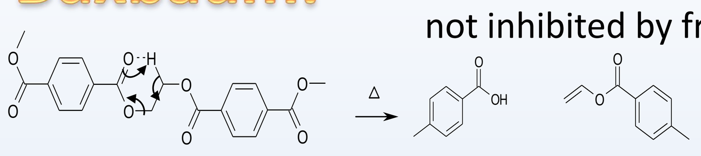
- No exhaustive literature can be found regarding the PET carbonization mechanism.
- Disagreements exist about the primary chain-scission mechanism due to thermal degradation.
- Only Holland and Hay have provided a study of the structural evolution of PET charred solid residues during thermal or thermoxidative degradation.

AIM: Identify which of the mechanisms reported in the literature are relevant to PET thermal decomposition, thus providing an integrated mechanism for both volatilisation and charring of PET in the combustion process by a detailed molecular characterization of the volatiles and of the residues produced by thermal degradation . The results of this work can be useful for designing fire retardants for PET.

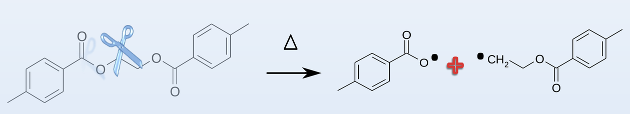
LITERATURE BACKGROUND[1-7]

? It is still not clear whether heterolytic or homolytic scission of aliphatic fragments is **the first step of degradation.**

Buxbaum: **Heterolytic reaction**: thermal degradation was not inhibited by free radical trapping agents.



Bounekhel and McNeill: To explain the overall presence of several degradation products, they suggested ester bond **homolytic cleavages.**



ONLY Holland and Hay:

They provided an explanation for the solid residue structural evolution during the PET carbonization, analyzing the IR spectra changes related to the characteristic aromatic structure signals.

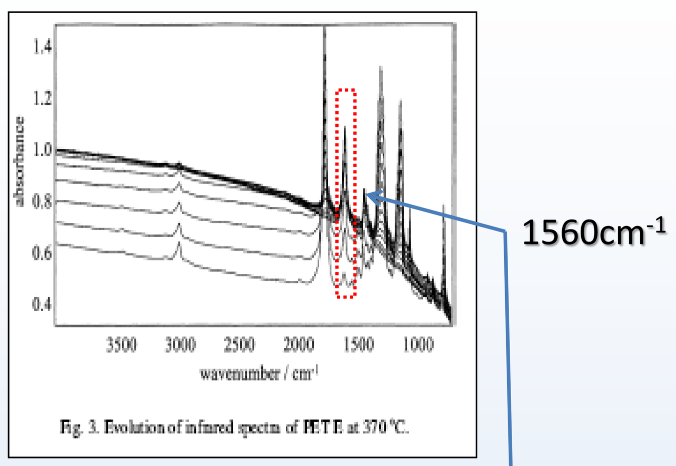


Fig. 3. Evolution of infrared spectra of PET at 370 °C.

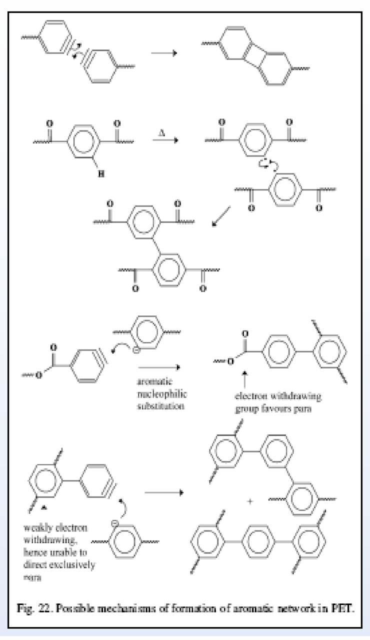


Fig. 22. Possible mechanism of formation of aromatic network in PET.

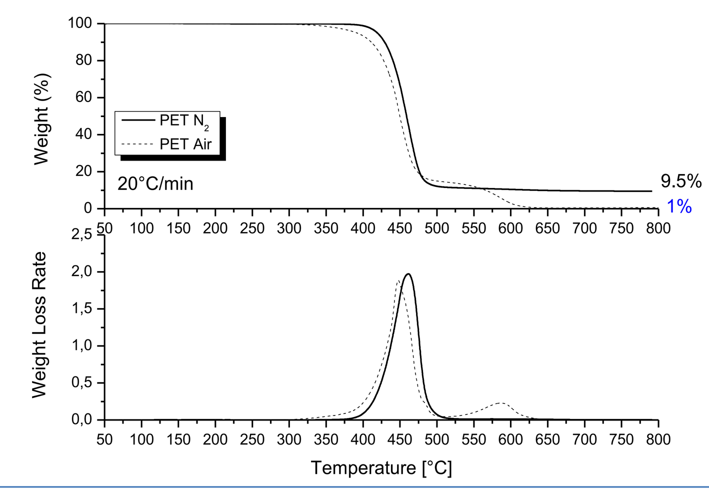
Build-up of conjugated aromatic structures

RESULTS PRESENTATION

Characterization approach

Particular attention was addressed to the **ANALYSIS OF CHARRED SOLID RESIDUE** structural changes by IR characterization at different temperatures of thermal degradation. Moreover, the hyphenated technique TG-IR has allowed the definition of the temperature ranges within which the volatile species evolved during the heating process adopted for the experiment. Based on the results obtained from TGA analysis on neat PET, pyrolysis experiments were performed at 375,400 and 425°C.

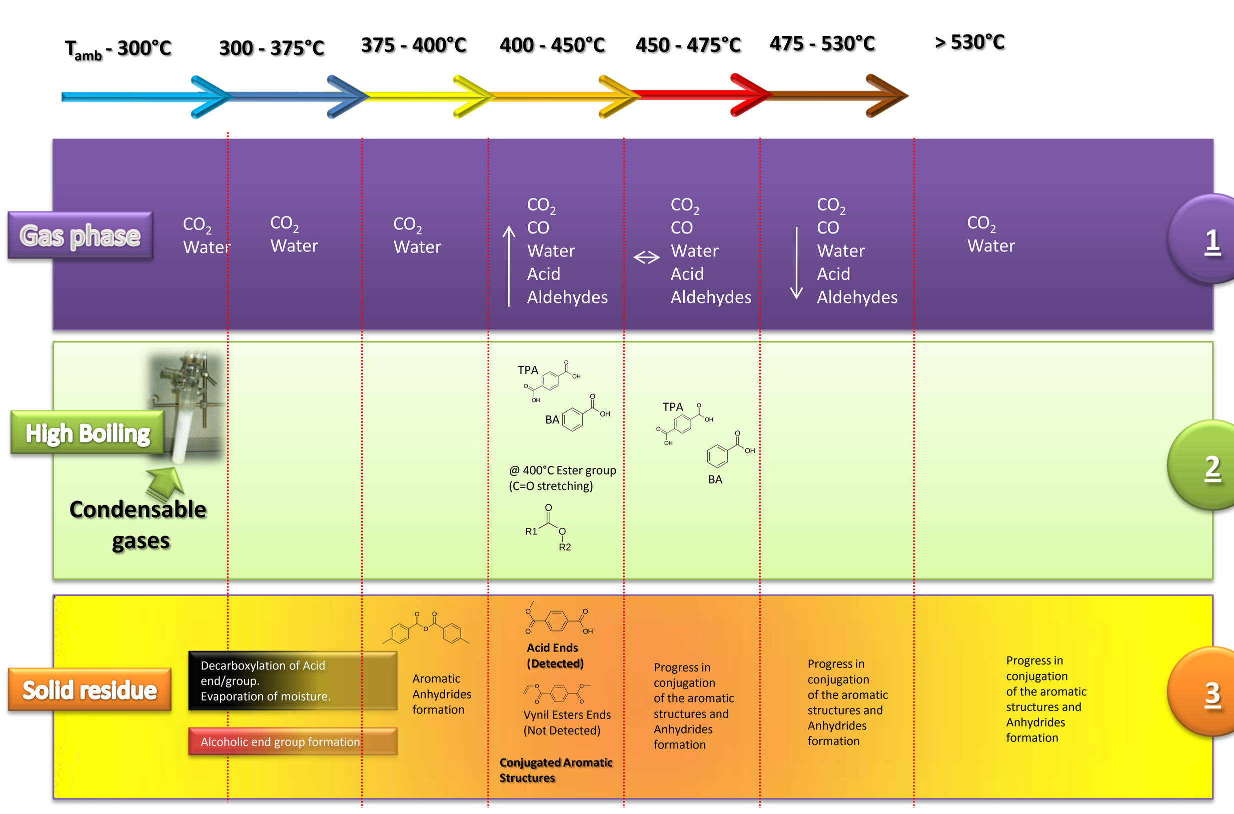
TGA of neat PET



Nitrogen
Single stage of thermal degradation. T_{max}= 450°C

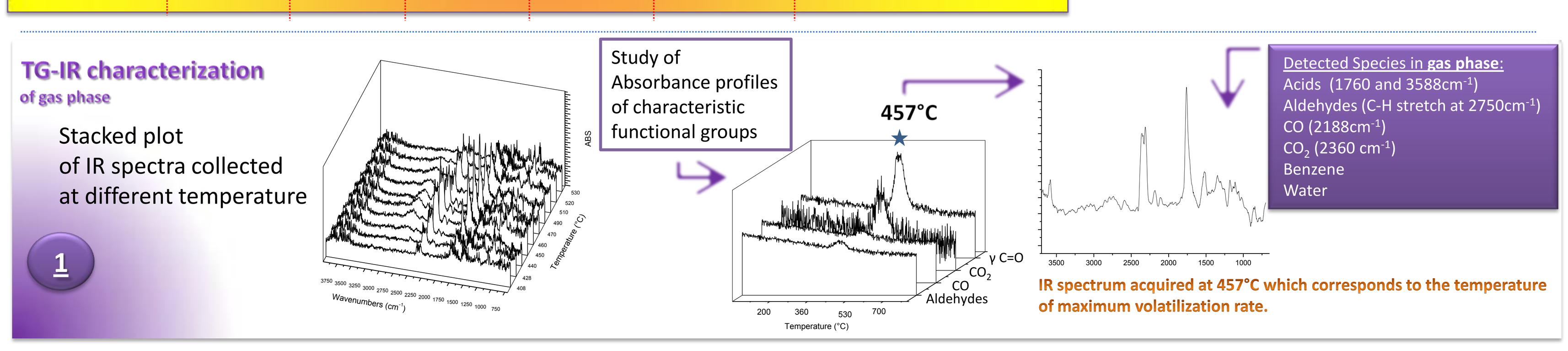
Air
Two stages of thermal decomposition.
@ 590°C: complete oxidation to volatile products of carbonization residues.

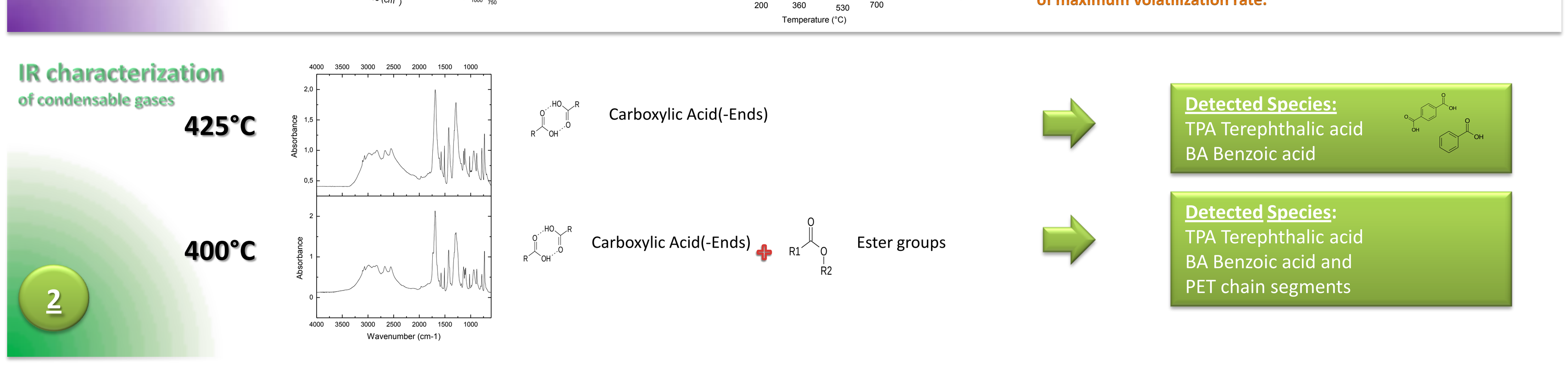
THERMAL DEGRADATION N_2

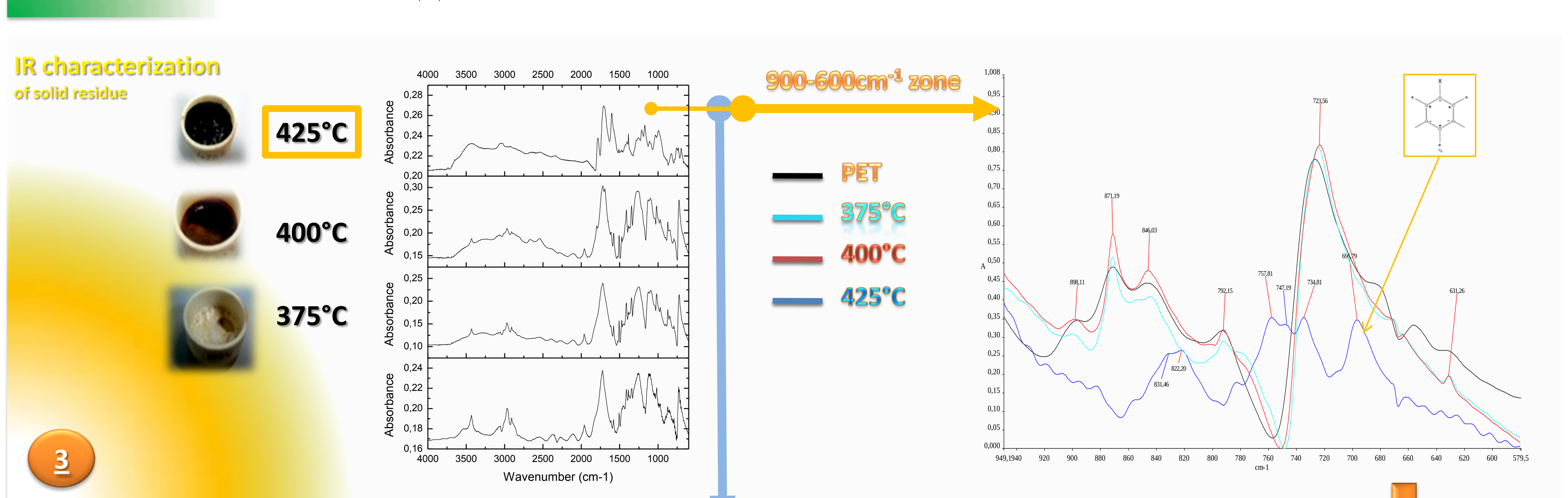


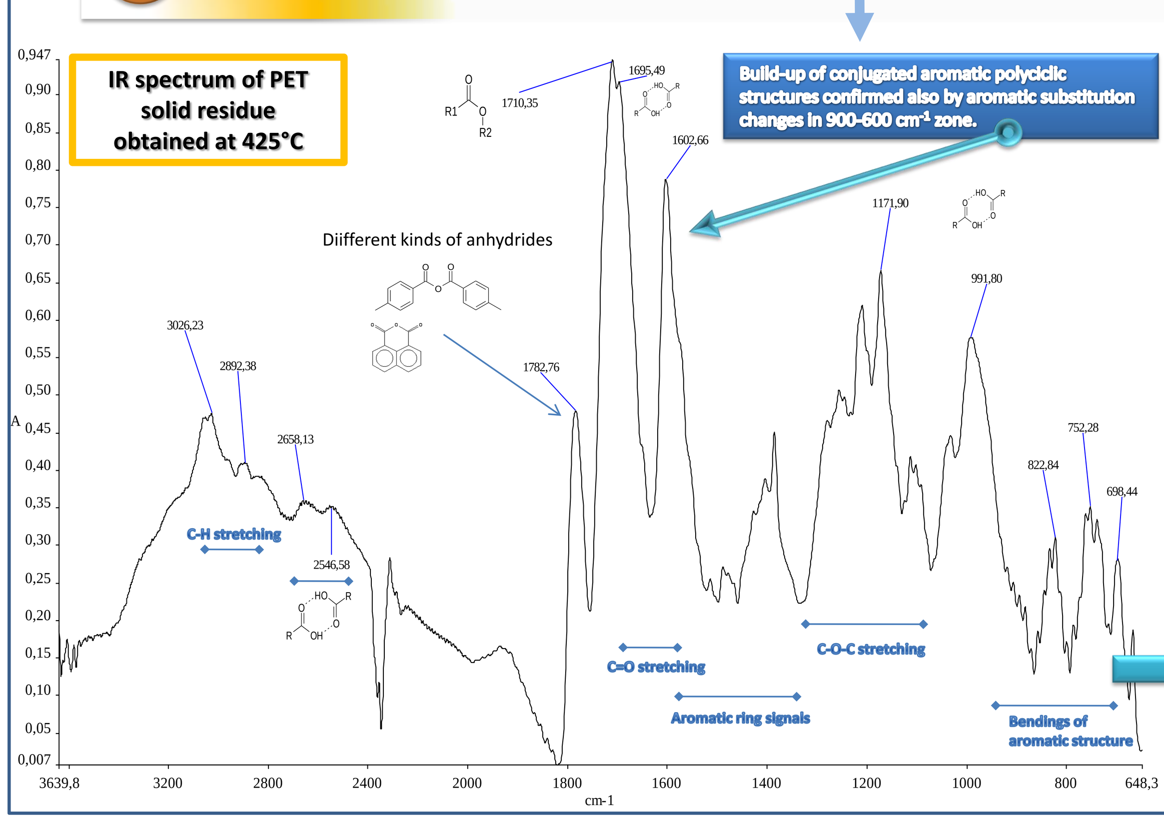
DIFFERENT TECHNIQUES HAVE PERMITTED TO DETECT THE SPECIES PRODUCED IN THE THREE PHASES

1. The release of non condensable gases was monitored by IR spectroscopy during a TG-IR analysis.
2. The condensable gases were collected on the surface of the internal pyrolysator jacket.
3. IR spectra of solid residues obtained at different temperatures were collected.



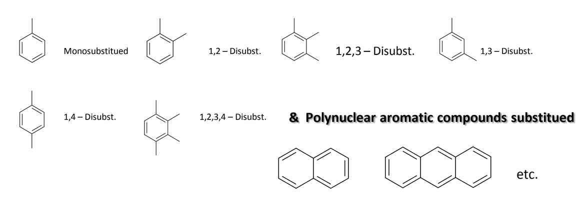






Comments:

Few structures have Puckering signal at 690cm⁻¹



Also the lack of signals of aromatic structures substituted in position 5 suggests the presence of conjugated aromatic systems.

The withdrawing effect of ester groups has as a consequence the deactivation of orto and para position for the electrophilic aromatic substitution, but at the same time it results in the activation of nucleophilic substitution.

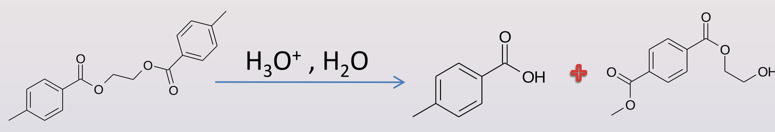
CONCLUSION: Hypothesis of mechanism N_2

To hypothesize a mechanism of PET residue thermal degradation the greatest difficulty lies in the comparison of literature data that was provided by different thermal degradation approaches. The authors have focalized their attention on the final solid residue structure depicting paths of hetero or homolytic degradation.

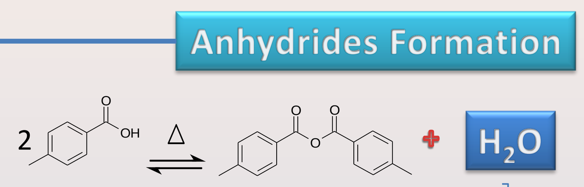
In fact it is known that for the gas phase pyrolysis more common is an Ei mechanism and radical reactions dominate the process. However, for polymers where the pyrolysis takes place in condensed phase, E2 and E1 mechanisms are not excluded. A type of mechanism which involves a cyclic transition state, which may be four-,five- or six-membered could be accompanied by radical reactions at the same time.

Acid-catalyzed Hydrolysis ROLE

As the temperature rises, the acid- catalyzed Hydrolysis becomes more evident. It is a well known phenomenon that leads to the formation of Acid and Alcoholic Ends.

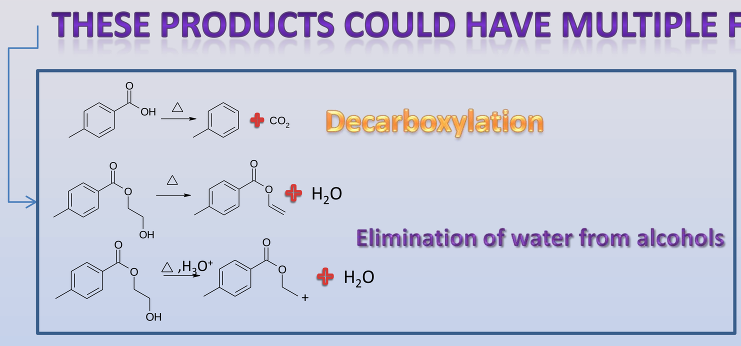


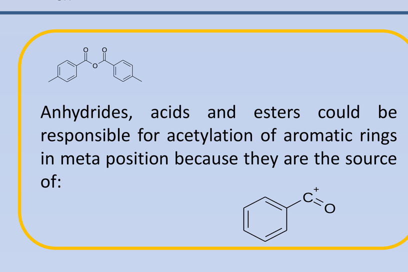
Anhydrides Formation

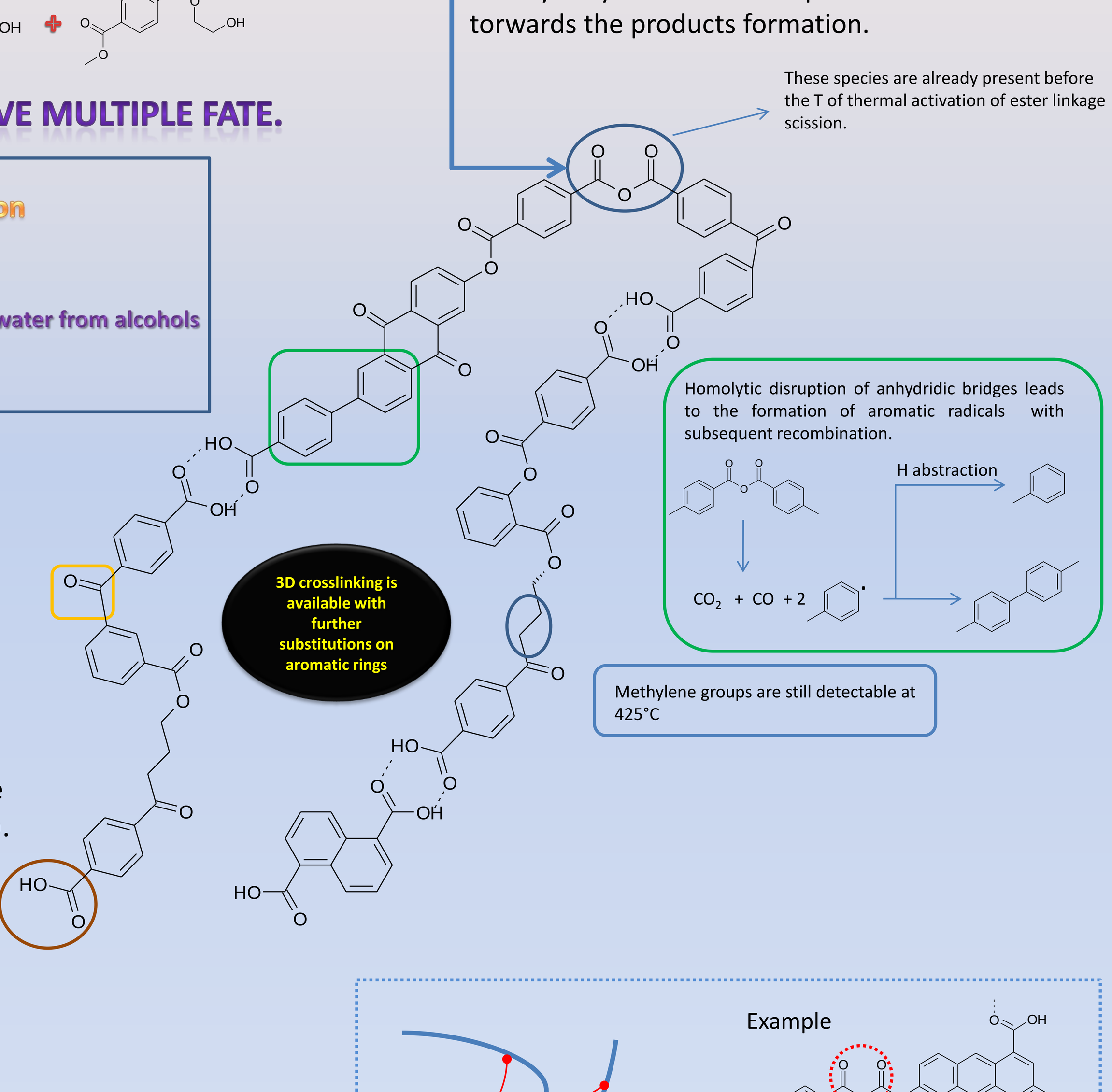


The Hydrolysis moves the equilibrium towards the products formation.

THESE PRODUCTS COULD HAVE MULTIPLE FATE.

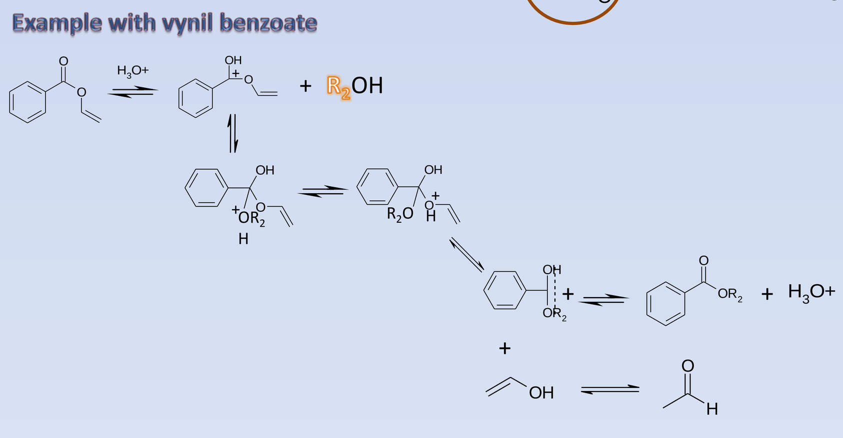


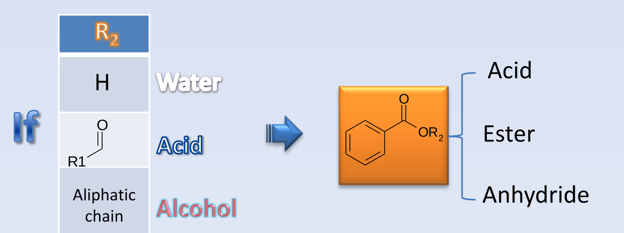


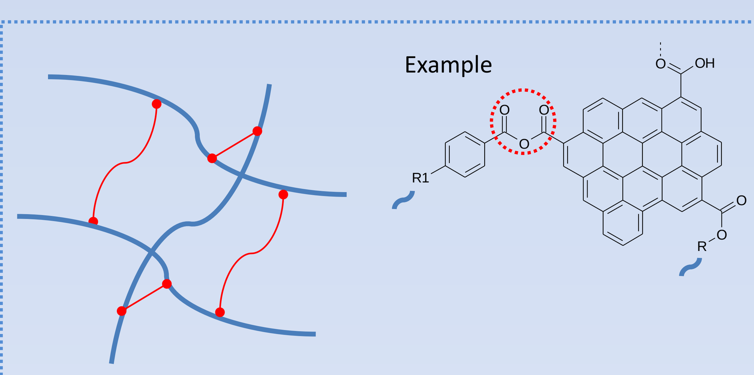


The Acid-Ends could be formed by Hydrolysis or extrusion of Acetaldehyde from vynil benzoate (transesterfication).

Transesterification
Example with vynil benzoate







Chain segments
Bridge Groups (Anhydrides, Ketones, Ester etc.)

The IR signal at 1600cm⁻¹ is usually related to the build up of conjugated aromatic systems. It is reasonable **to ponder also on the conjugation of aromatic structures with carbonyl groups of ketones, acids, esters and anhydrides.** The condensation of aromatic rings is accompanied by the crosslinking of linear chain segments which does not break the conjugation between the aromatic domains.

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