

Summary notes on the organic chemistry of polymers and polymerisation

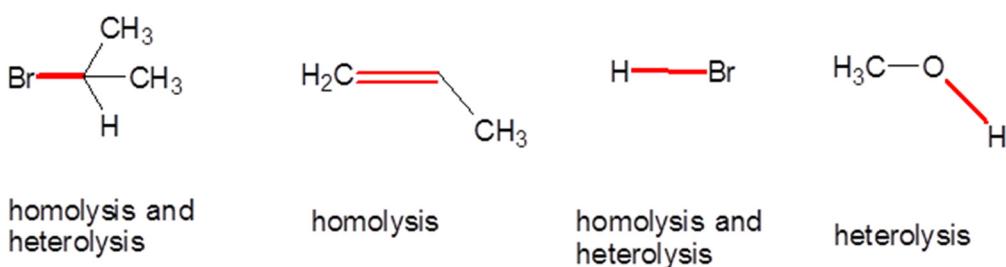
Breaking and making bonds

- Bonding involves sharing two electrons between two atoms. In organic chemistry, this typically means between carbon and another element such as hydrogen, nitrogen etc. Carbon because of its ability to hybridise and because of the electronic configurations of these hybrids is able to form single, double and triple bonds with itself and other elements.
- During a chemical reaction, these bonds are broken and reformed to make the products.
- Organic chemists use “curly arrows” to represent the movement of electrons during a reaction to form the product. There are two types: one with a normal arrow head and one with half an arrow head (sometimes described as “fishhooks”). The first represents two electrons moving, the second represents a single electron, however, in this case there will always be two arrows.



- When a bond is broken **heterolytically**, the pair of electrons in the bond moves to one of the two atoms creating positive and negative charges. The electron pair will move to the most electronegative atom.
- When the bond is broken **homolytically**, one electron from the bond goes onto one of the atoms, the other moves towards the other atom.
- In polymer chemistry we make and break lots of bonds.

Exercise – draw the arrows and break the following bonds (play with it – what makes sense?)



Polymerisation starts with monomers

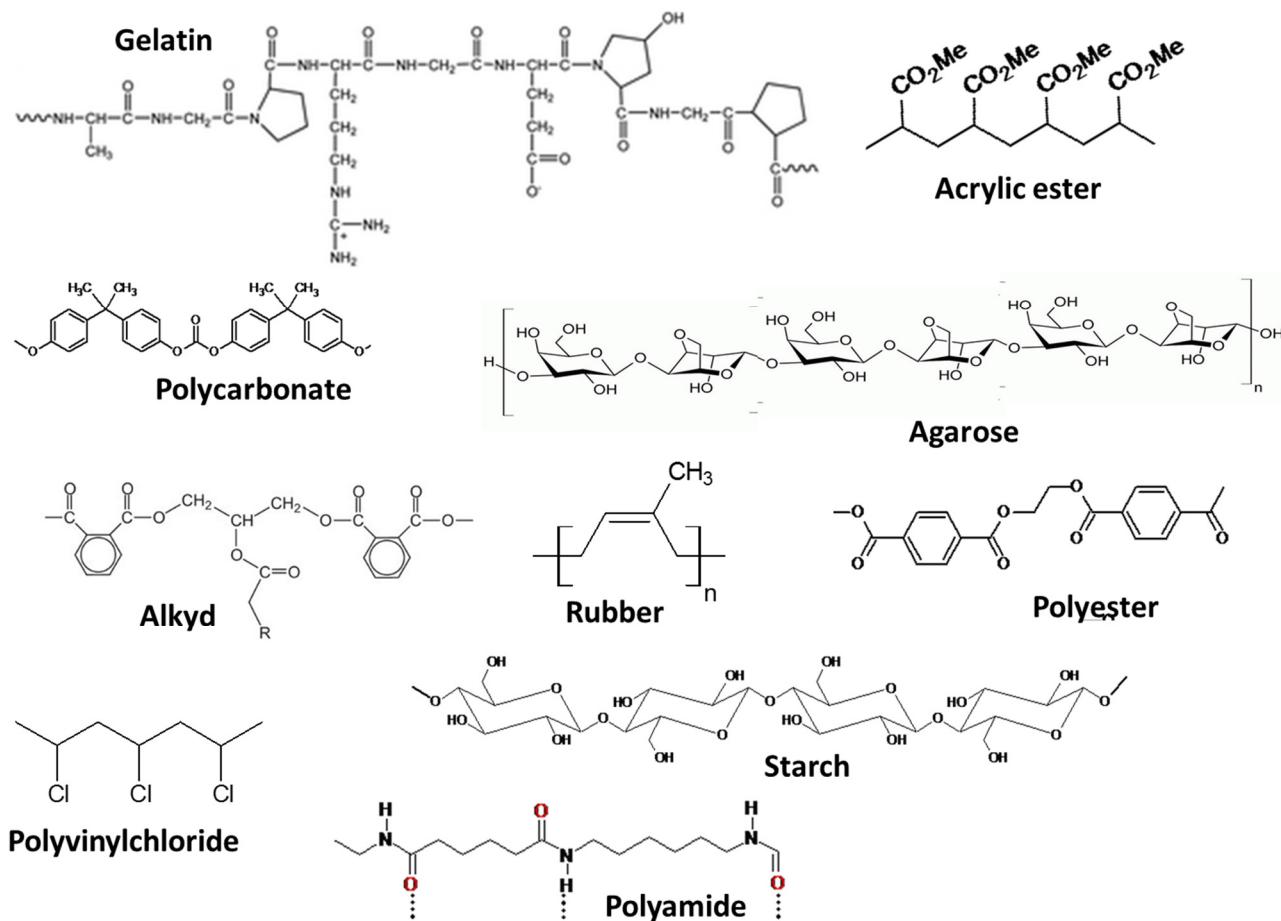
- To make a polyester, we need a selection of monomers which can undergo an ester condensation reaction: an organic acid (or equivalent) and an alcohol.
- To make nylon, which is a polyamide, we use an organic acid (or equivalent) and an amine. This is also a condensation reaction.
 - Which biological reaction is it similar to? (hint: think proteins)*

- To make polymers such as polypropylene or polystyrene we use propylene and styrene, respectively.
- While the principle is the same for all polymers: adding smaller molecules together in some way to make larger molecules, the chemistry and type of reactions occurring are very different.
- We need to remember some basic things about functional groups, how they react and the sorts of properties that they confer on the molecule.

Functional groups in polymers

Identifying functional groups in polymers can give us clues as to how they are made.

- Can you recognise the functional groups in the following polymers?
- What types of monomers are present?
- Which of these are natural? Which are man-made?

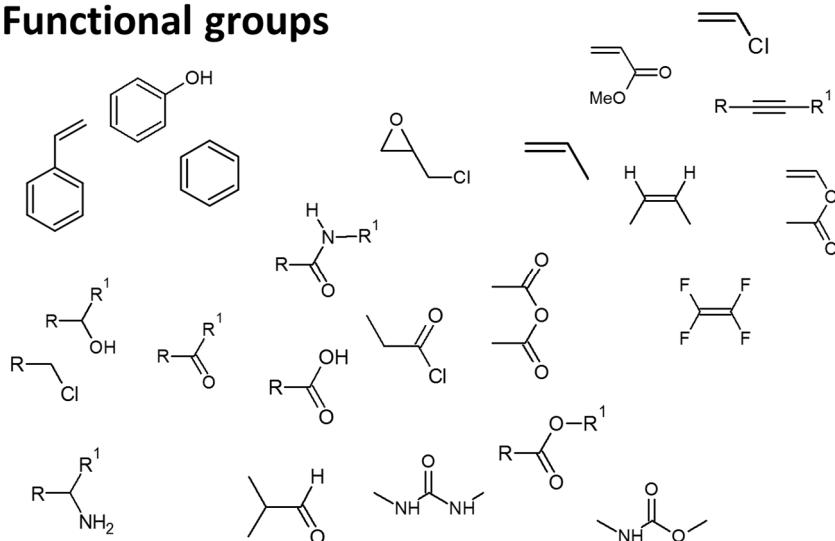


Polymers can be classified in different ways:

• Chemistry	• Functional groups • Bonds formed	• Derivation	• Synthetic • natural
• Chemistry mechanism	• Addition • Condensation	• Composition	• Homopolymers • Copolymers
• Processing	• Thermoplastics • (hard-soft) • Thermosets • (soft-hard)	• Physical characteristics	• Plastic • Elastomer

Some typical functional groups found in polymers:

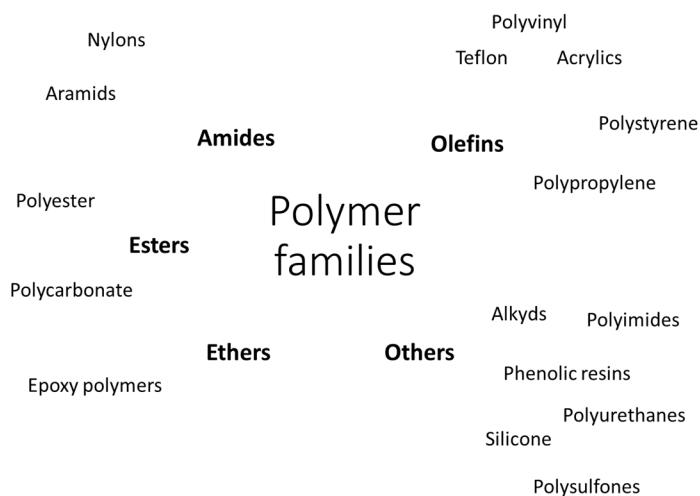
Functional groups



Polymers from monomers

- By playing with different factors in the reaction, we can make polymers with desired properties.
 - Stoichiometry of mixtures of monomers
 - Rates of addition, Temperature, Concentration, Catalysts, Additives

Families of Polymers:

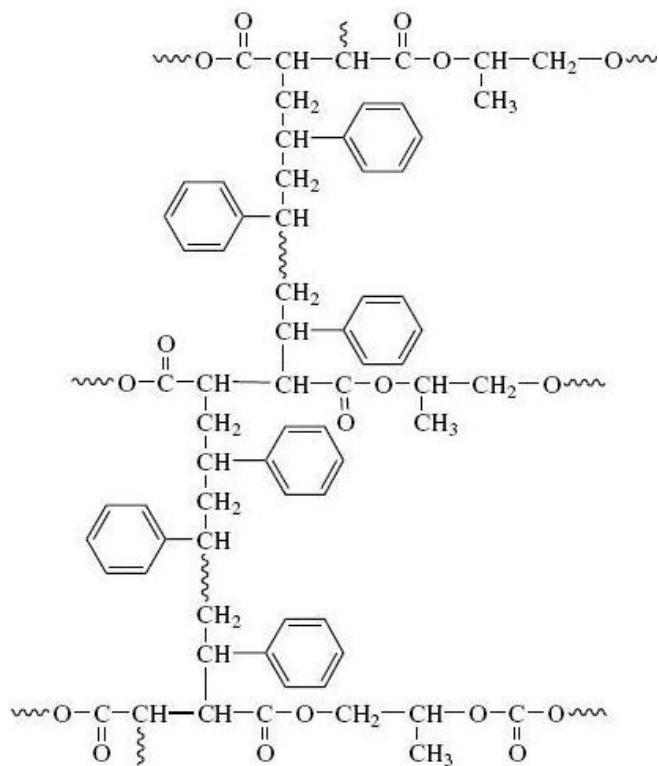


Types of reactions in polymer chemistry

- Polymer chemistry is vast, however, the types of reactions involved are relatively few. The most important reactions at this level are:
- **Condensation** reactions
- **Radical addition** reactions
- Each of these has its own particular characteristics.
- We will illustrate both, using the example of making a styrenated polyester resin which uses both types of reaction in a sequence to form the final product which has excellent physical properties.

Case study: styrenated polyester resin

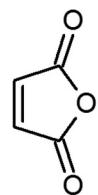
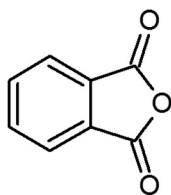
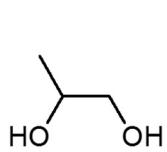
- This type of polymer has a broad range of everyday uses because it possesses excellent structural properties: resistance to abrasion, strength, durability and stability, particularly when mixed with other materials such as glass-fibre and stone.
- The structure looks complicated, however, if we look closely we can identify some common functional groups and these can give us a clue as to how it is made.
- Exercise: have a look at the structure below which is part of a styrenated polyester resin: which functional groups can you recognise?



- This polymer is made in two separate phases because the chemistry required in each is very different. The first step is making the polyester backbone, the second step is making the links between the polyester chains using polystyrene.

The First Phase: condensation

- The monomers present in the first step are:

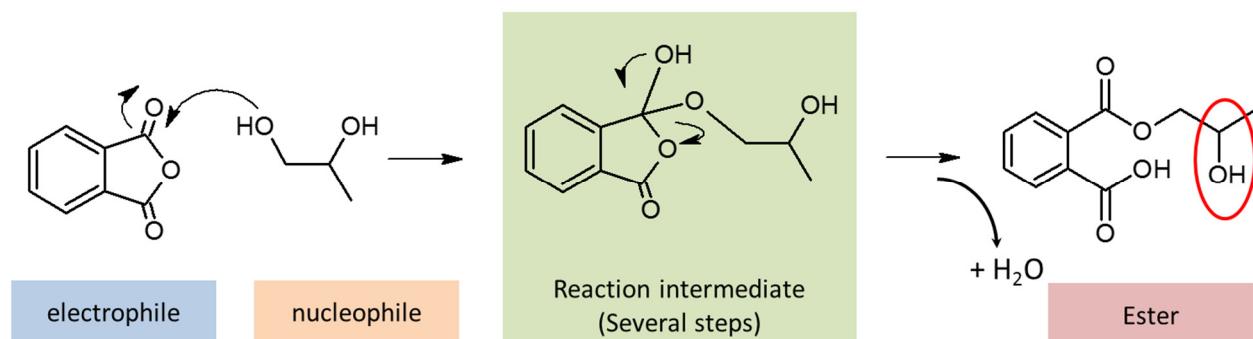


Propylene glycol

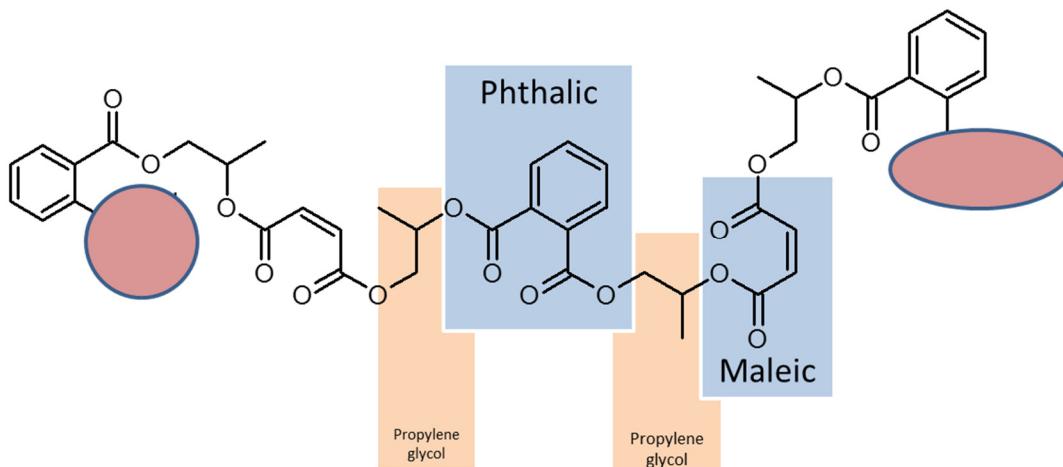
Phthalic anhydride

Maleic anhydride

- Note: the anhydride is used because it makes the C=O more reactive than if we simply used the carboxylic acid.
- The nucleophilic alcohol group on the propylene glycol attacks the anhydride group of the phthalic anhydride to make an ester. This is a condensation reaction which releases water.
- Since each ester has an additional nucleophilic hydroxyl and each acid has two possibilities for reaction, the result is a polymeric chain.



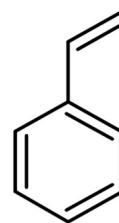
- The product of the condensation step is the polyester chain which has malate and phthalate groups distributed along it at random.



The second phase

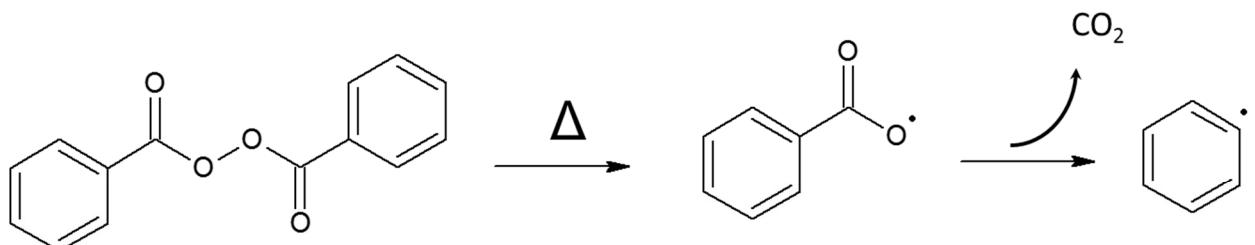
- To prepare a polymer with the desired properties, the second step involves *linking the chains together*.

- This is done using a *radical addition reaction* to the *double bonds of the maleic units* present in the polymer chains.
 - It is an example of a *radical polymerisation* which takes place through three well-defined steps although the mechanism for each may be complex
 - The three main steps:
 - Initiation
 - Propagation
 - Termination
 - The condensation polymer from the first part is dissolved in *styrene and* added along with a catalyst (e.g. cobalt). The reaction is heated slightly



Styrene

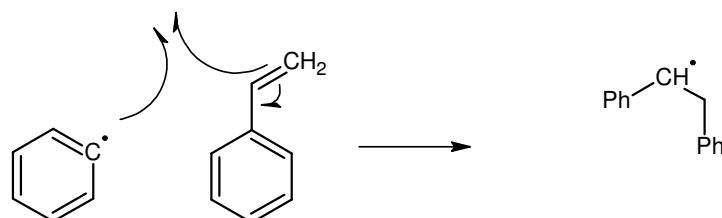
Initiation



Benzoyl peroxide

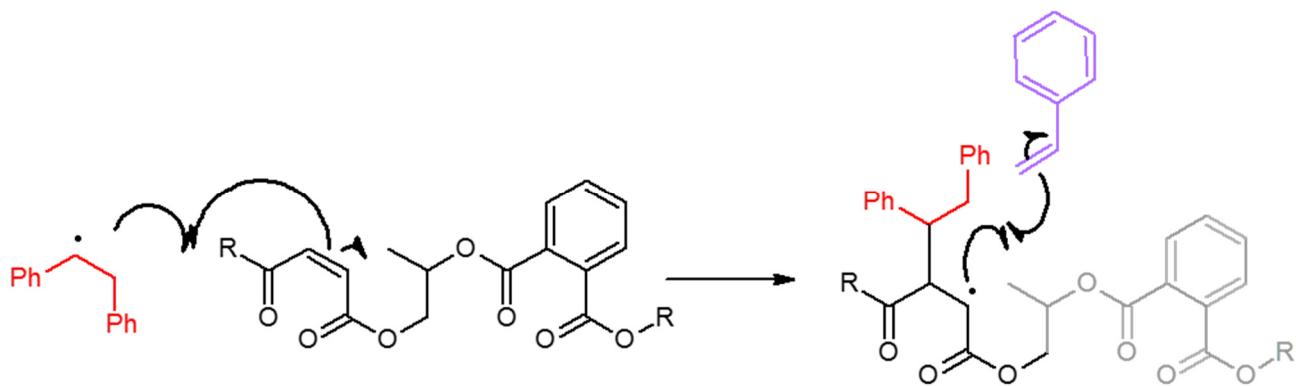
Phenyl radical

- The heat breaks the weak O-O bond of the benzoyl peroxide *initiator* in a *homolytic* fission and the benzoyl radical loses CO₂ to give a phenyl radical – this starts the cross-linking reaction

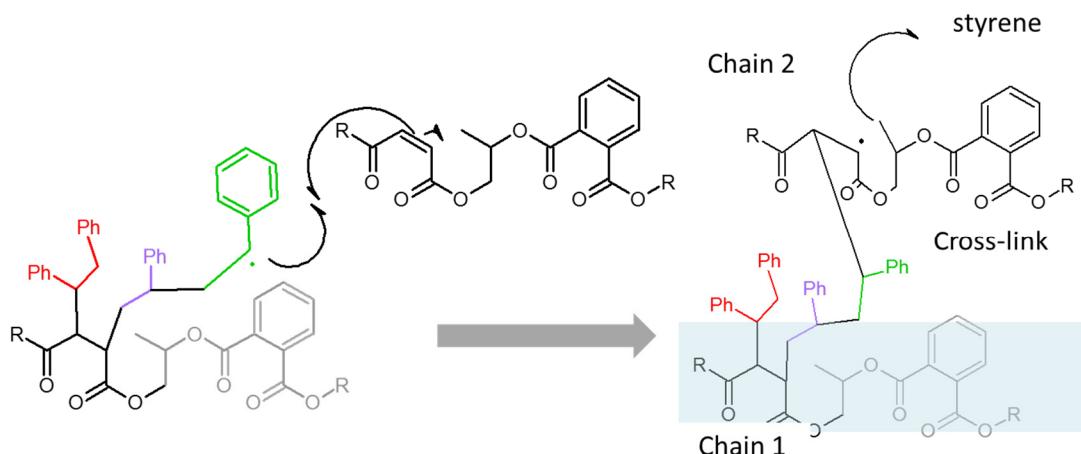


Propagation

- The phenyl radical reacts with styrene to form an intermediate radical which reacts with the chain of the condensation polymer.

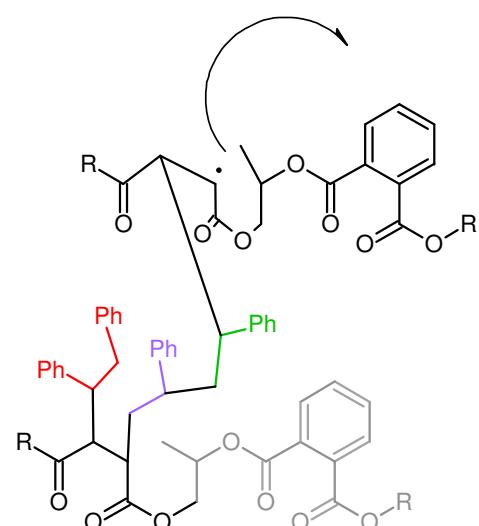


- The radical adds to a maleic double bond on the polymer
- This generates a radical on the polymer chain
- This reacts with another molecule of styrene to generate a further radical. Until the radical meets a maleic double on another polymer chain which closes the cross-link, however, the radical still exists....
 - *Why does the radical form on the carbon nearest the styrene ring?*



Termination

- The reaction stops here!
- Termination happens when two radicals combine to give a non-radical species
- This can be “head-to-head” where the radical reacts with a radical on another chain or it could be a disproportionation (which is a bit more complicated)



What are the main differences between the types of chemistry in the two phases?

(Hint: Think about the types of chemical species involved in the reactions)

Vocabulary

Term

Activated carbonyl (“active ester”)
 Catalysis – catalyst – catalytic - catalyse
 Chain
 Cleavage – cleave = break
 Condensation
 Copolymer
 Cross-linking agent/ reagent
 Curly arrows
 Electron pair – lone pair – anion
 Electrophile – electrophilic - accept
 Fission = break = split
 Glycol = diol
 Half-arrows
 Heterolysis – heterolytic
 Homolysis – homolytic
 Initiation – initiator - initiate
 Leaving group (=nucleofuge)
 Maleic anhydride
 Mechanism
 Monomer
 Nucleophile – nucleophilic – attack
 Phthalic anhydride
 Polymer
 Polymerisation
 Propagation- propagate
 Radical – abstraction - abstract
 Stages
 Styrene
 Termination - terminate

Phonetic transcription

/'æktrɪ'veɪtɪd ka:bəʊnayl (‘æktrɪv ‘estə’) /
 /kə'tælɪsɪs – ‘kætəlɪst – ,kætə'lɪtɪk - kə'tælæs /
 /tʃeɪn /
 /'kli:vɪdʒ – kli:v = breɪk /
 /konden'seɪʃən /
 /Kəʊplɪmə /
 /krɒs-'lɪŋkɪŋ 'eɪdʒənt/ ri(:)'eɪdʒənt /
 /'kɔ:li 'ærəʊz /
 /ɪ'lektrɒn pəə – ləʊn pəə – ænəɪən /
 /elekt्रəʊfəil - elektrəʊfɪlik - ək'sept /
 /'fɪʃən = breɪk = splɪt /
 /glaɪkol = dæiol /
 /ha:f-'ærəʊz /
 /heterolɪsɪs - həterəʊlɪtɪk /
 /həʊmlɪsɪs - həʊmlɪtɪk /
 /ɪ'nɪʃ'eɪʃən – i'nɪʃeɪtə - i'nɪʃeɪt /
 /li:vɪŋ gru:p (=nju:kli:əʊfju:dʒ) /
 /Mæleik æn'hædraɪd /
 /'mækənɪzm /
 /məʊnəmə /
 /nju:kli:əʊfaɪl - nju:kli:əʊfɪlik – ə'tæk /
 /fθælɪk æn'hædraɪd /
 /'pɔɪmə /
 /pə,lɪmərəɪ'zeɪʃən /
 /prəpə'geɪʃən- 'prəpəgeɪt /
 /rædɪkəl – æb'strækʃən - 'æbstrækt /
 /stɪədʒɪz /
 /stairi:n /
 /tɜ:mɪ'neɪʃən - 'tɜ:minɪet /