CR39 – processo di etching per monitoraggio Rn

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- **Uno sguardo generale alle proprietà chimico-fisiche di CR39**
- **Cenni sull'interazione radiazione materia: effetto specifico in CR39**
- **Processo di etching anisotropo in NaOH: rivelare le tracce da ionizzazione**

CR39… why??

La plastica CR 39 si chiama così perchè è stata prodotta con successo dalla Columbia Resin nel 1940 dopo 38 tentativi andati male!

Il materiale di cui sono costituite le lenti, il CR39, ha origine a metà del XX secolo.

In quel periodo si cercava un valido sostituto del vetro, con cui erano realizzate tutte le lenti dell'epoca. In un primo momento, si era optato per l'utilizzo del Polimetilmetacrilato (comunemente chiamato plexiglass) ma aveva una scarsissima resistenza ai graffi.

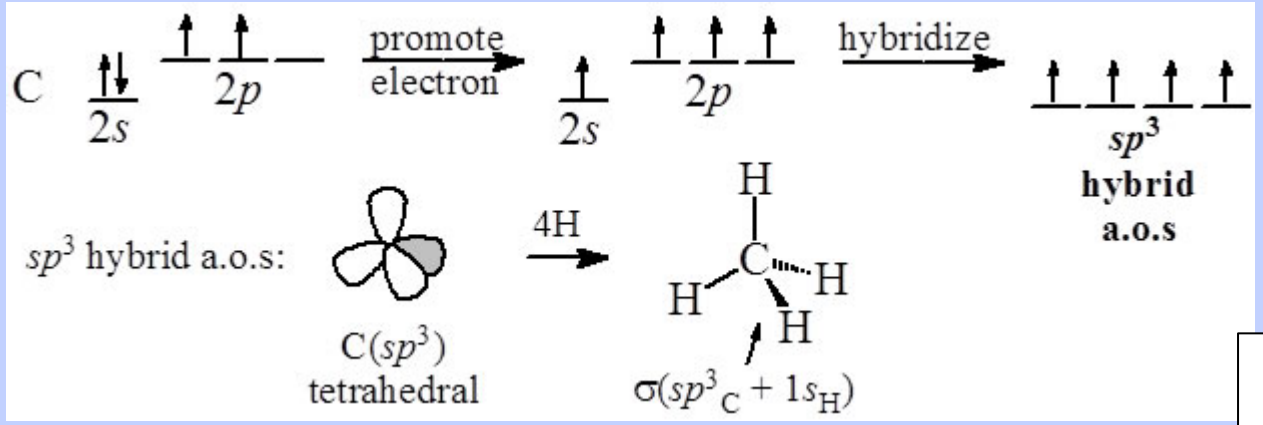
Su richiesta del governo americano, l'azienda Columbia Resin fu incaricata di creare un nuovo materiale al fine di realizzare i parabrezza degli aerei militari. Furono progettati circa 180 monomeri termoindurenti, tra i quali fu scelto il 39°. A questo nuovo materiale fu dato il nome di Columbia Resin 39 o CR39.

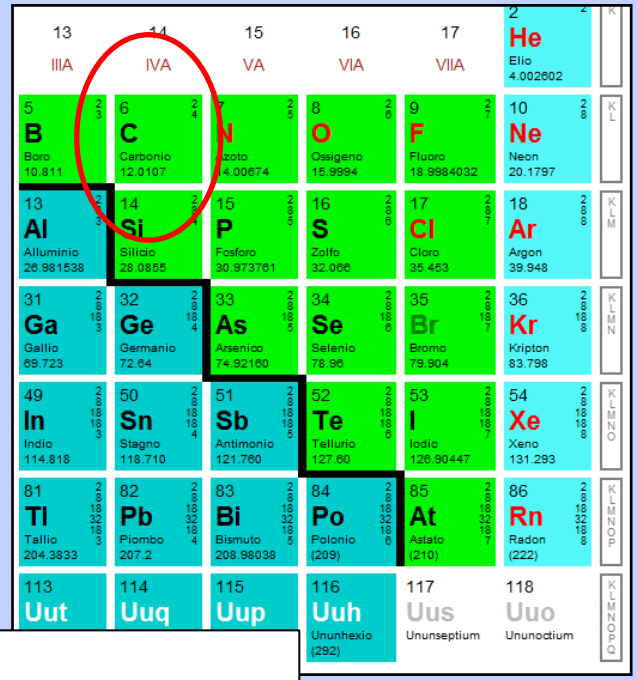
Nel 1947 Robert Graham, un optometrista, intuì le enormi potenzialità di questo materiale al mondo delle lenti oftalmiche. Da quel momento in poi le lenti in CR39 divennero lo standard del settore.

Radiolab

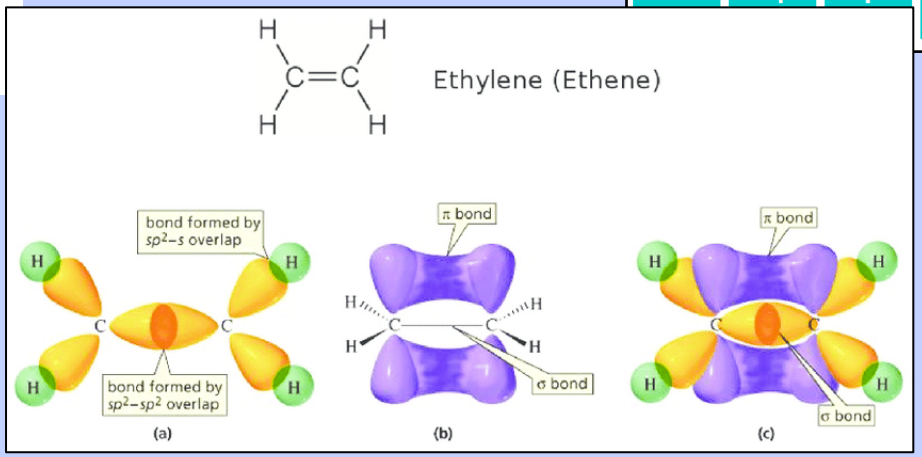
Carbon

Carbon has 4 electrons ⟹ It will realize 4 single bonds

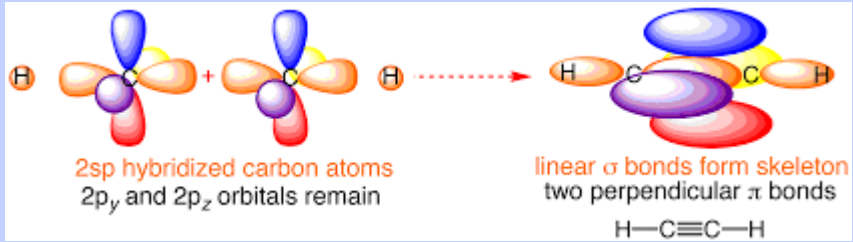




But also 1 double bond and 2 single bonds



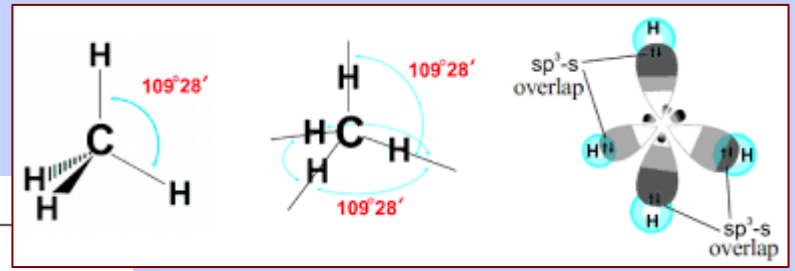
But also 1 triple bond and 1 single bond



Ethyne

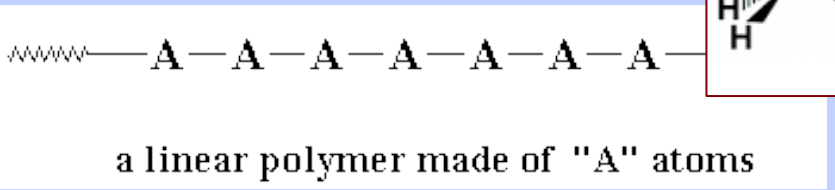
Radiolab

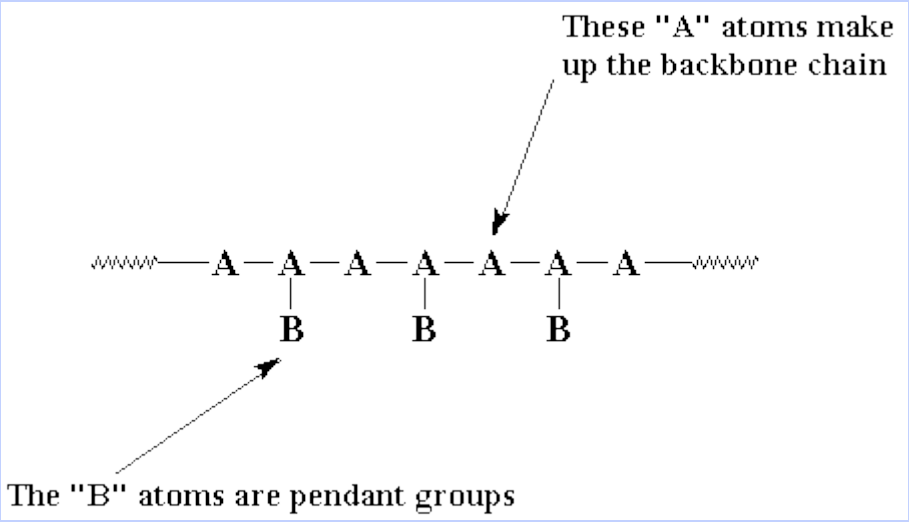
In general… C in polymers is sp^3

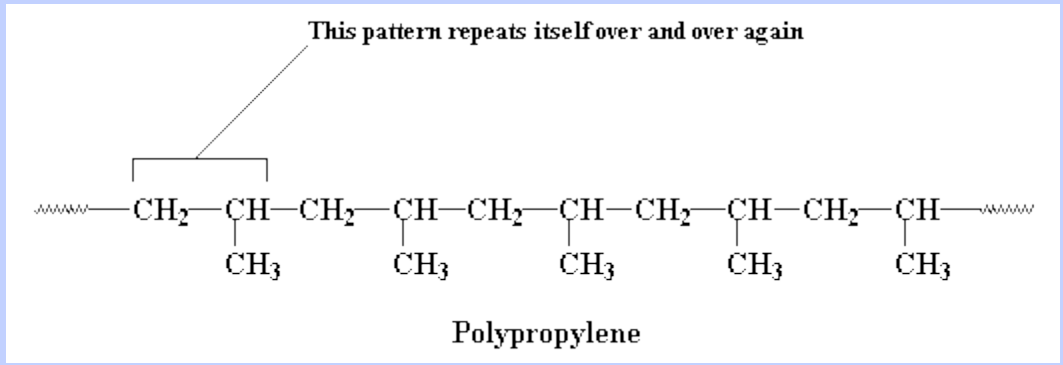


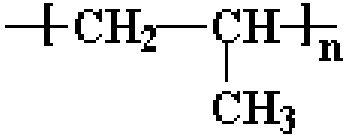
Polymer…from greek… MANY

Monomer…from greek…ONE









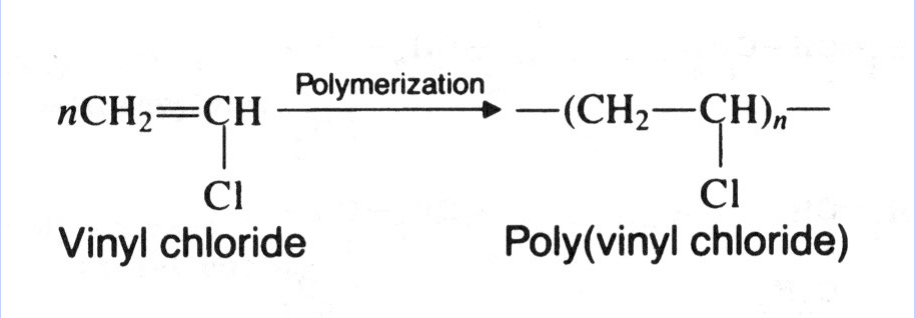
n= degree of polymerization

Radiolab

Polymerization processes

Chain-growth polymerization: a polymerization in which monomer units are joined together without loss of atoms

for example:



from the perspective of the chemical industry, chain-growth polymerization is the single most important reaction of alkenes

Radical: a molecule or ion containing one or more unpaired electrons

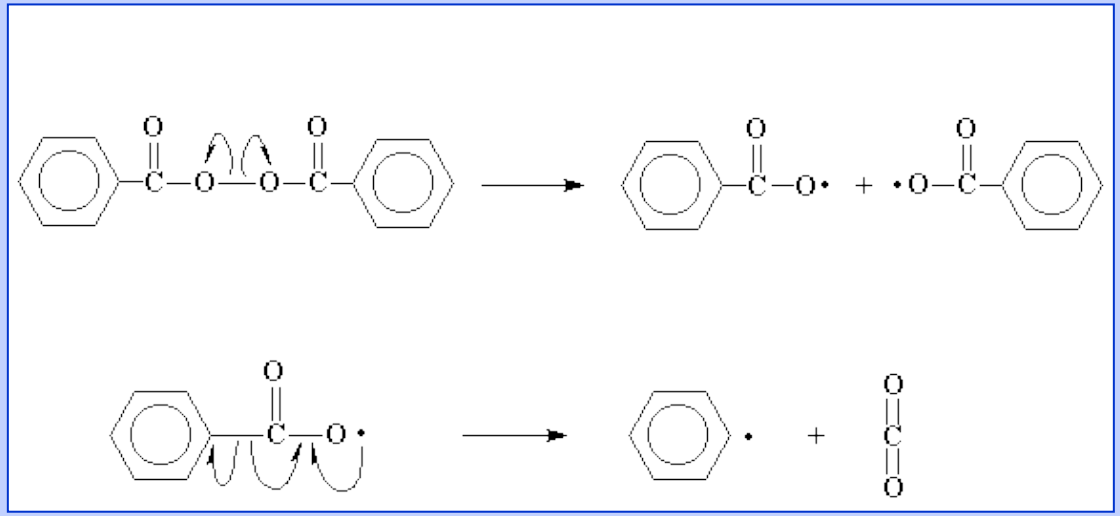
To account for the polymerization of alkenes in the presence of peroxides, chemists propose a three-step radical chain mechanism

(1) chain initiation

(2) chain propagation

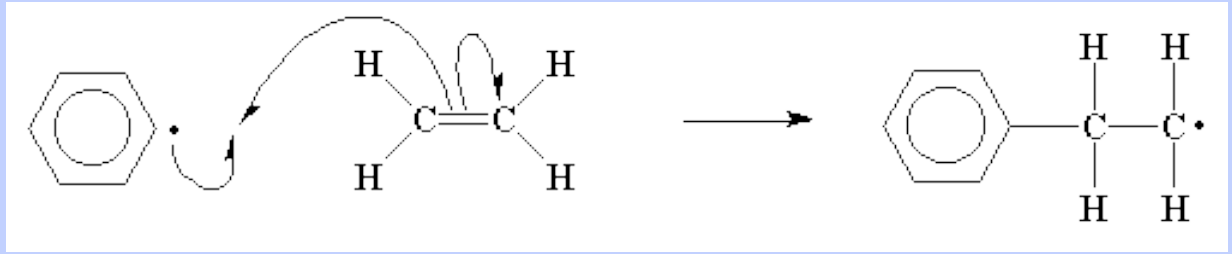
(3) chain termination

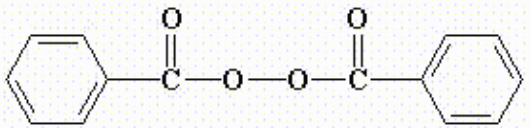
Step 1: INITIATION a molecule with a labile bond undergoes scission and divides in two free radicals (through heating or UV irradiation)



Benzoyl peroxide undergoes bond scission in two steps, thus forming two phenyl radicals extremely reactive…they will attack any electron rich molecule to restore the electron couple

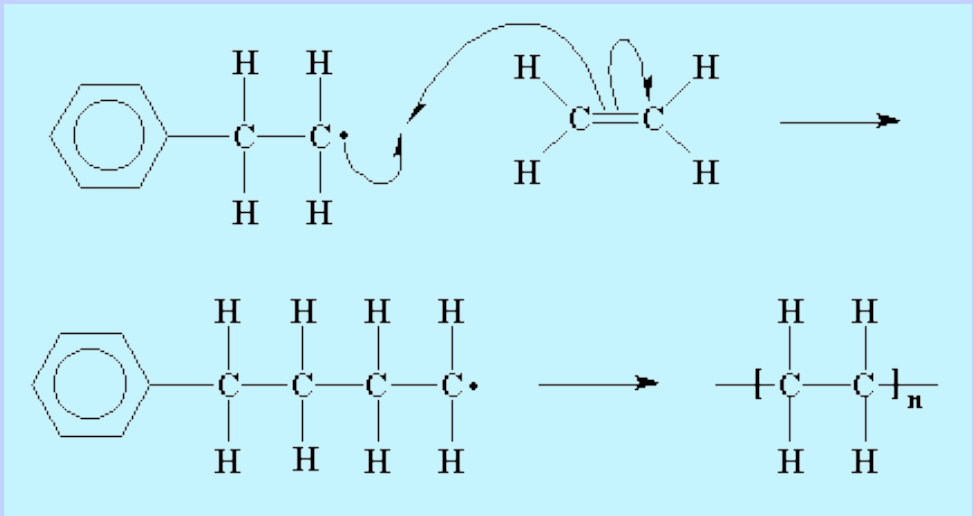
In the case of polyethylene, the radical atta
bond (thus rich in electrons!), the double bon
formed, at the same time…





Step 2: chain propagation

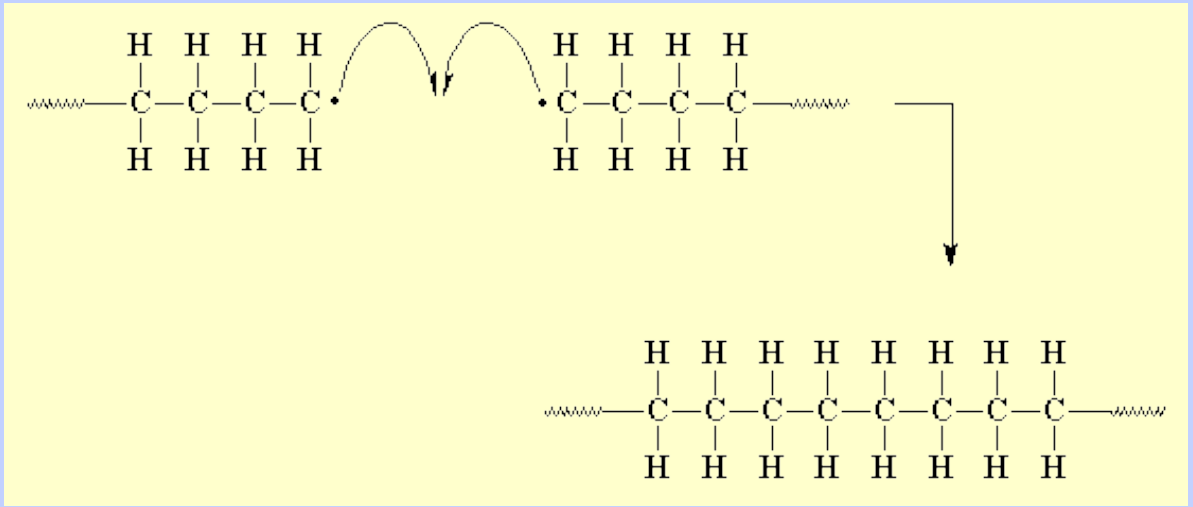
- a step in a radical chain reaction characterized by the reaction of a radical and a molecule to give a new radical
- Chain length, n: the number of times the cycle of chain propagation steps repeats in a chain reaction



The reaction proceeds until monomer molecules available for attack are present…. But it comes to a halt when two macroradicals meet and couple, forming a complete and stable macromolecule. This can happen in different ways...

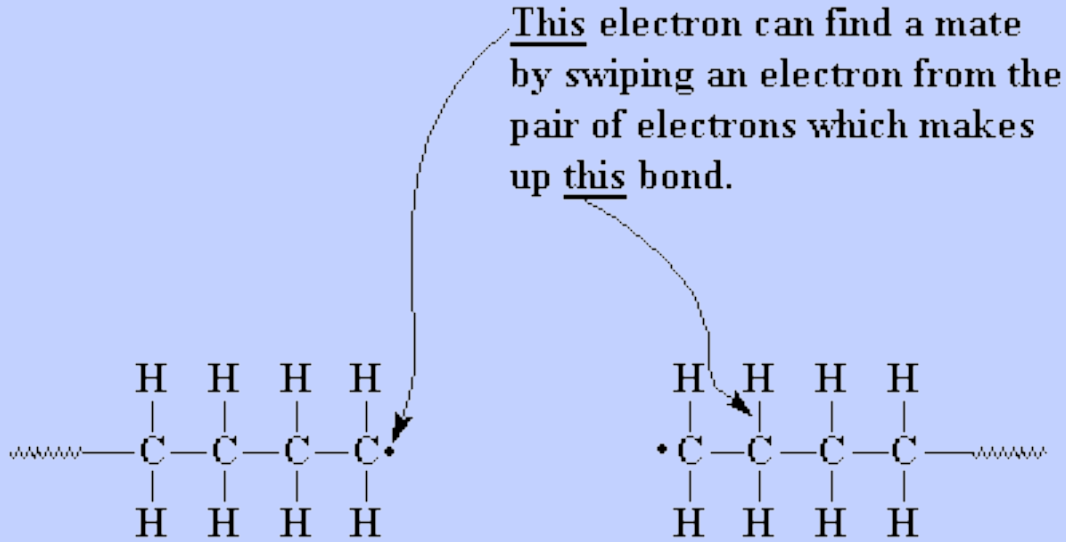
Step 3: chain termination

- a step in a radical chain mechanism that involves destruction of radicals
- one type of chain termination is radical coupling (**combination**)

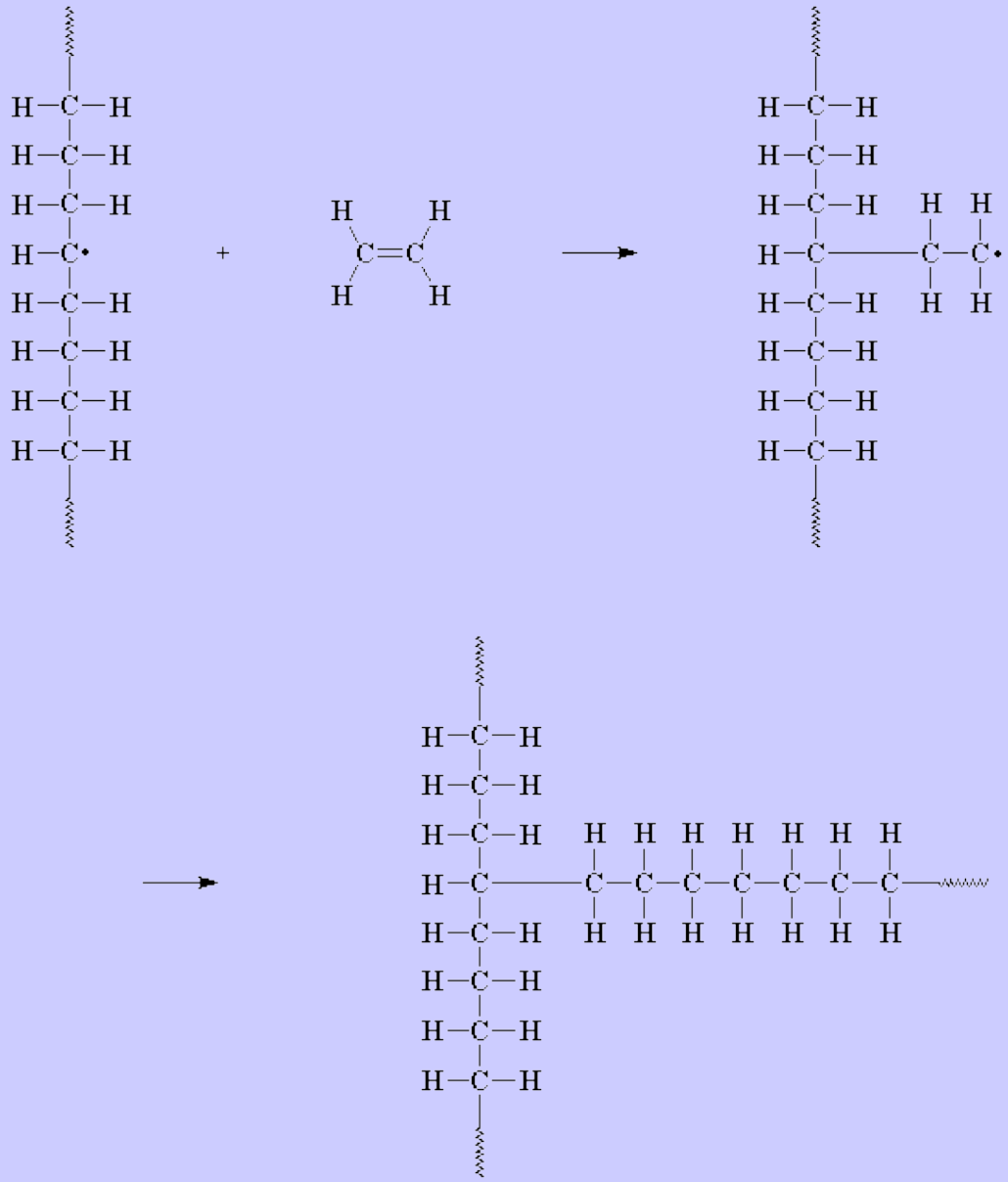


The second process is called **disproportionation** and it is much less intuitive…

The radical on a growing macromolecule meets another radical end, but instead of coupling the radical causes the bond breaking of an adjacent C-H group

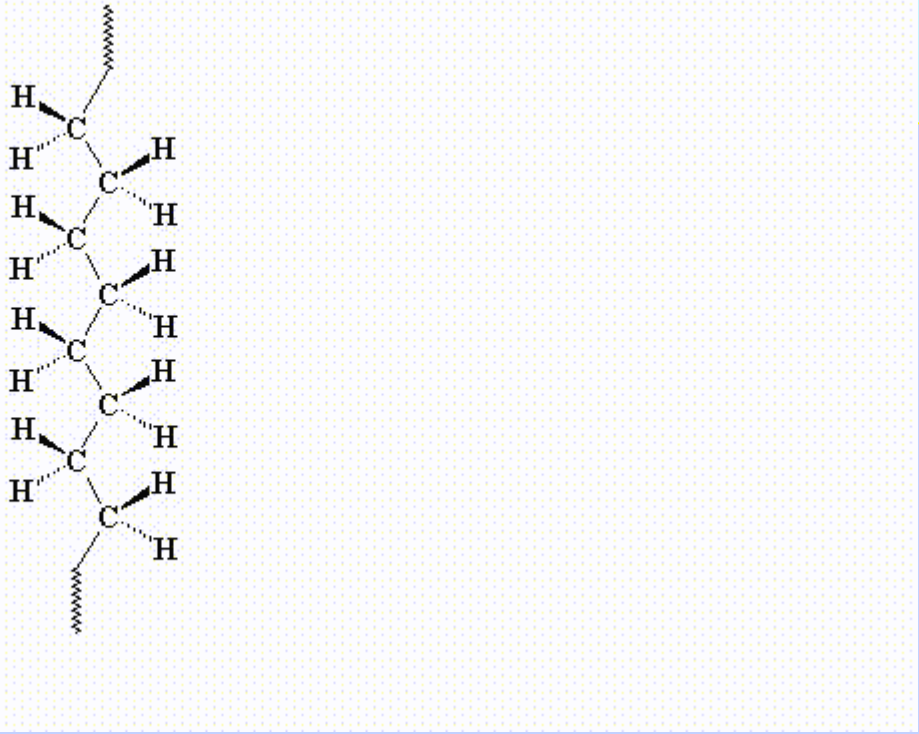


Consequences of chain transfer…….

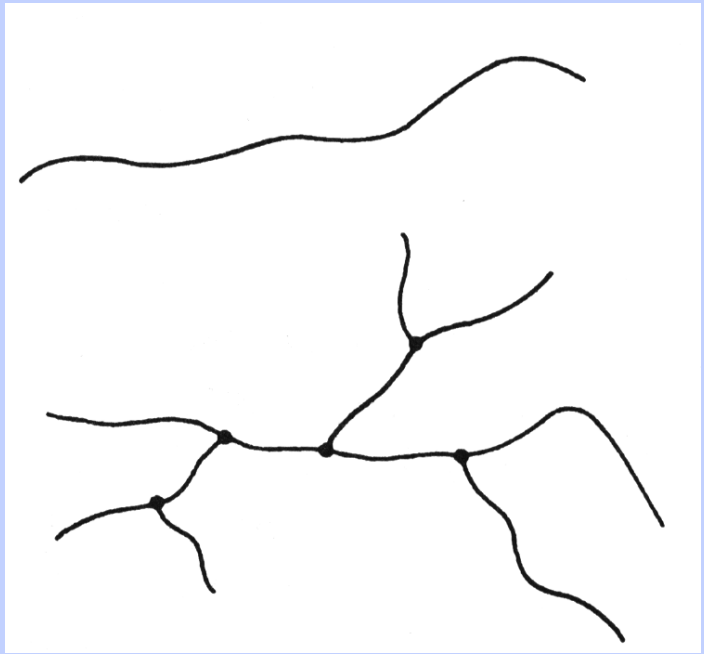


The reactivity of an end group is transferred from one chain to another, or from one position on a chain to another position on the same chain

- polymerization then continues at the 2° radical
- polyethylene formed by radical polymerization exhibits a number of butyl branches on the polymer main chain



The formation of a branched structure has dramatic consequences on the physical properties of the so produced polyethylene. In the case of branched structure only LOW DENSITY POLYETHYLENE will be obtained (LDPE). The structure not only affects the density but also the **degree of crystallinity,** which in turn affects several important technological properties of the product, as we will see... Linear PE can be obtained ONLY through **Ziegler-Natta polymerization**....

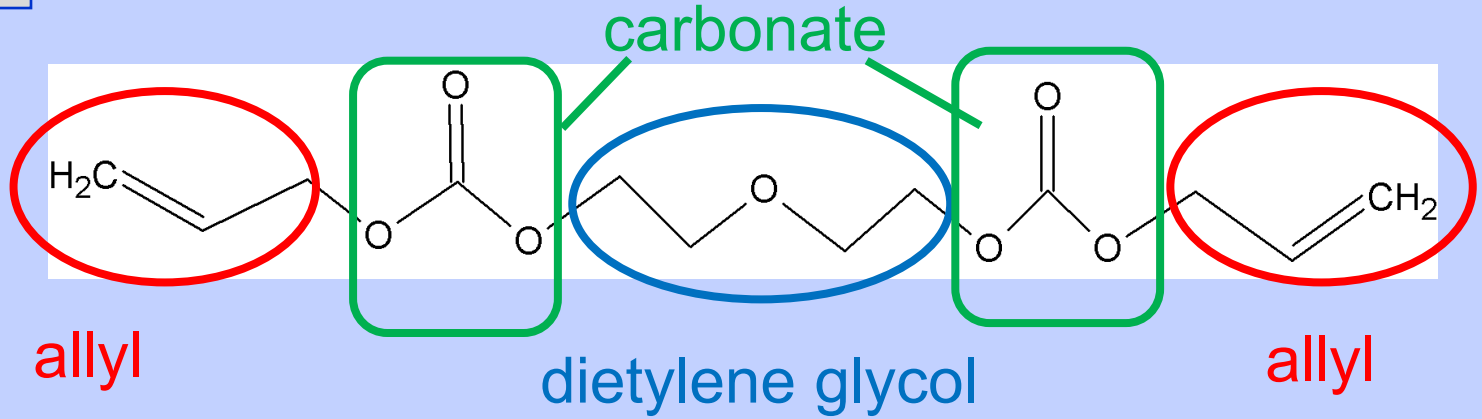


Linear

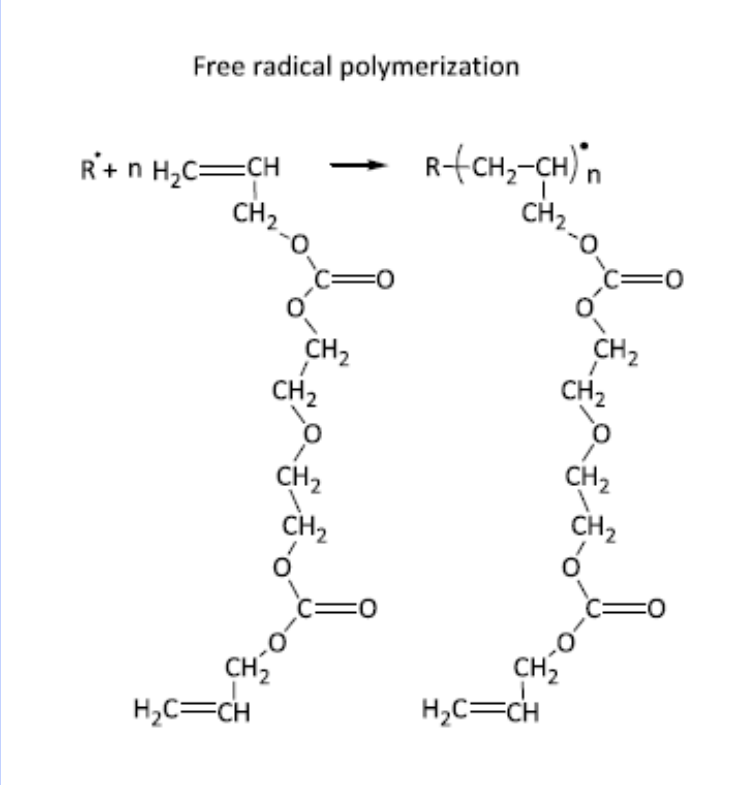
Branched

Il caso di PADC (CR39)

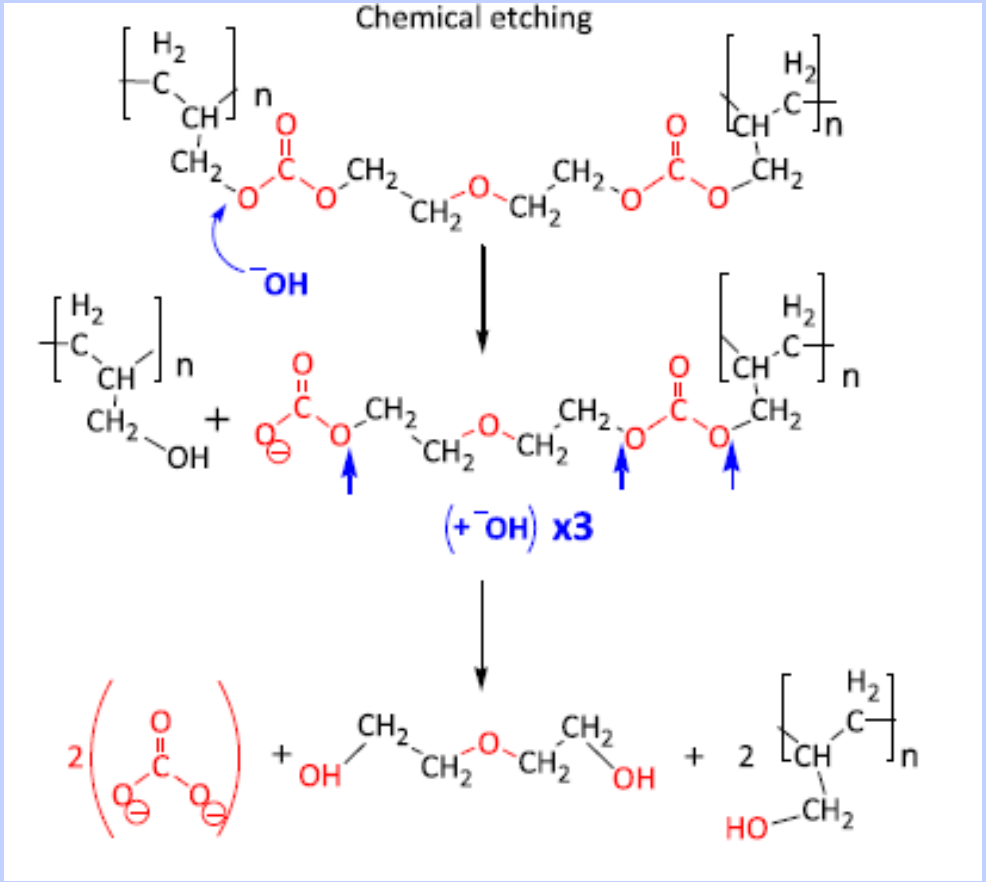
Il **MONOMERO**
allil dietilene glicole dicarbonato



dopo l'innesco con iniziatore BPO il doppio legame si rompe e ha inizio la reazione a catena



cosa succede al polimero con NaOH 6M a 80°C?



lo ione ossidrile OH^-

- è un **nucleofilo** : attacca i punti carenti di elettroni (δ^+) come il carbonio carbonilico C=O
- causa la rottura del legame C-O-C con formazione di dietilen glicole, ione carbonato $(CO_3)^{2-}$ e alcol poliallilico
- lo ione carbonato può decomporre rilasciando CO_2
- I prodotti della reazione di “etching” sono **solubili in acqua** dunque strato dopo strato il materiale si assottiglia

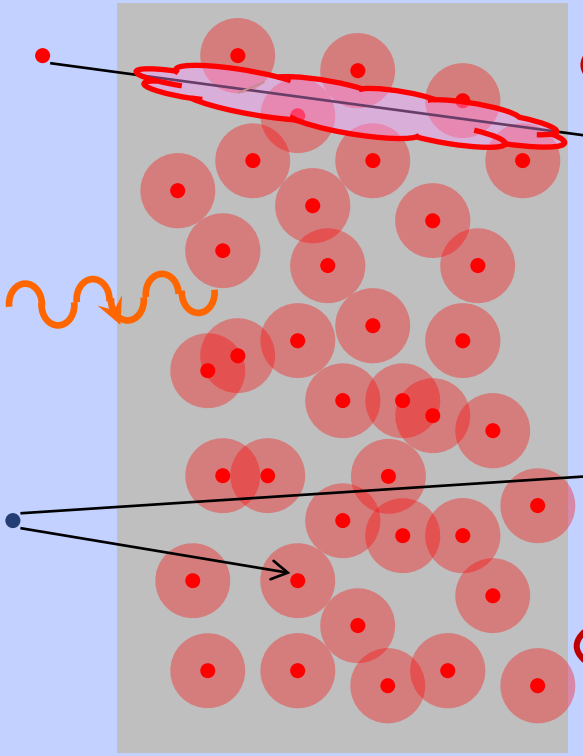
Radiazione e materia… possibili interazioni

Nel caso di materiali organici a basso Z e bassa densità

Charged particles (α, p)

Photons (UV, X-rays, γ)

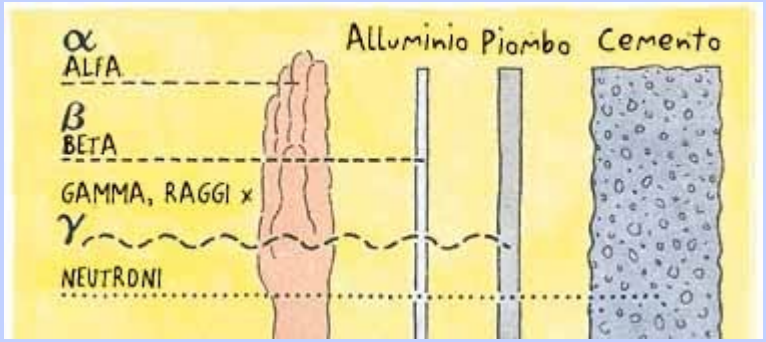
Neutral particles, n



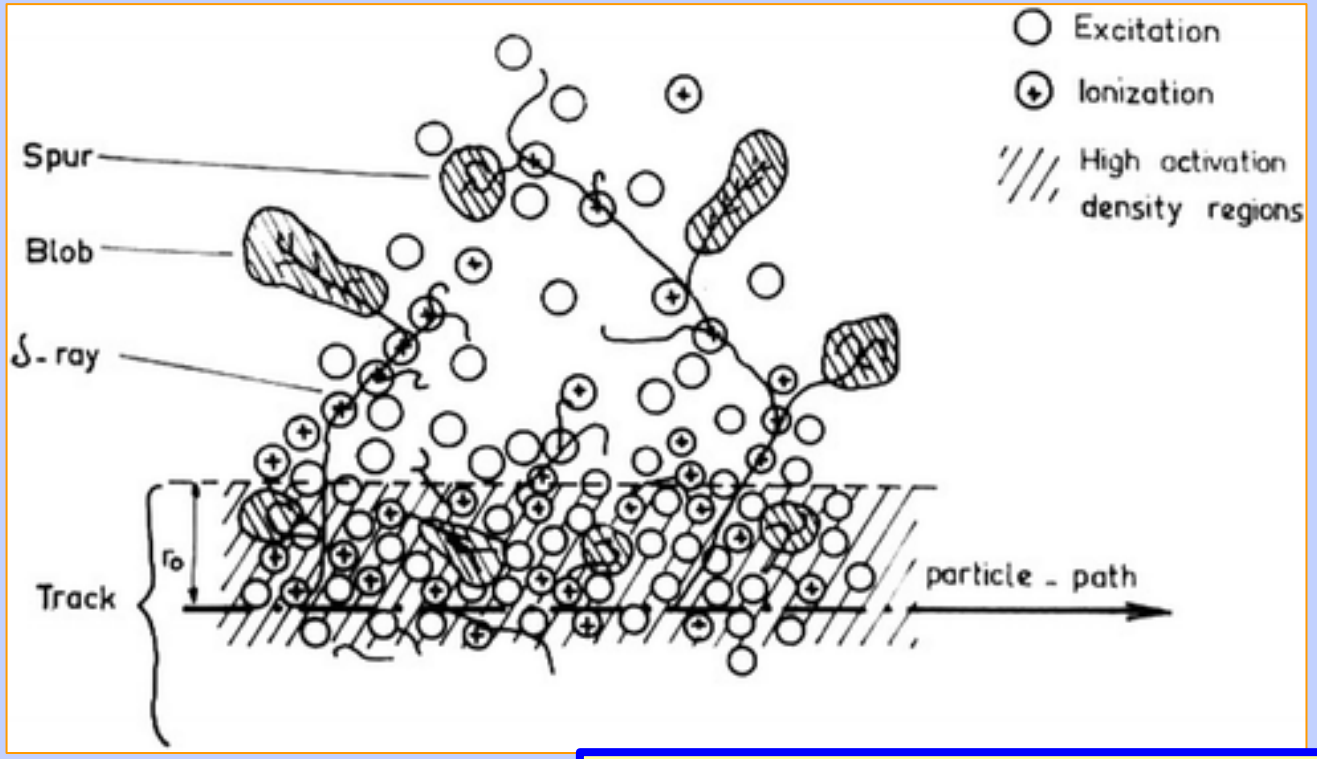
Ionization

Photoelectric Effect
Compton Effect
Pairs Generation

Nuclear collisions
(proton recoil) and
capture processes



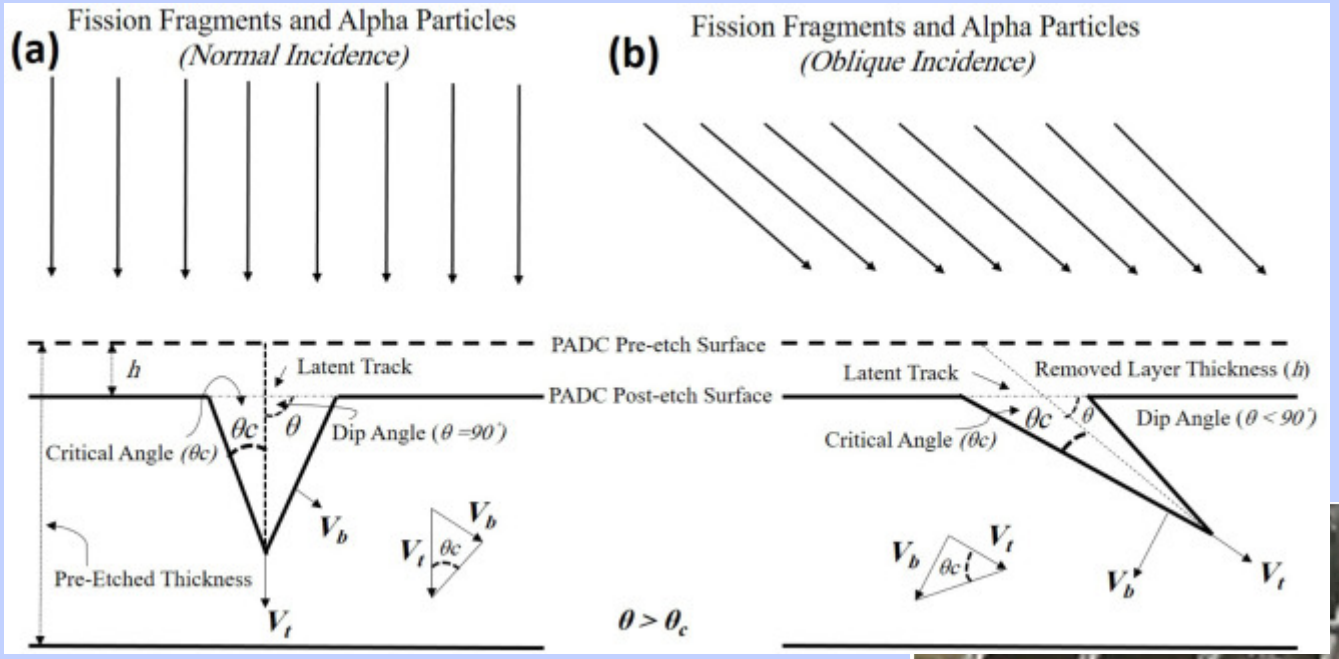
Nel nostro esperimento ci interessano le particelle alfa, dal decadimento di ^{222}Rn



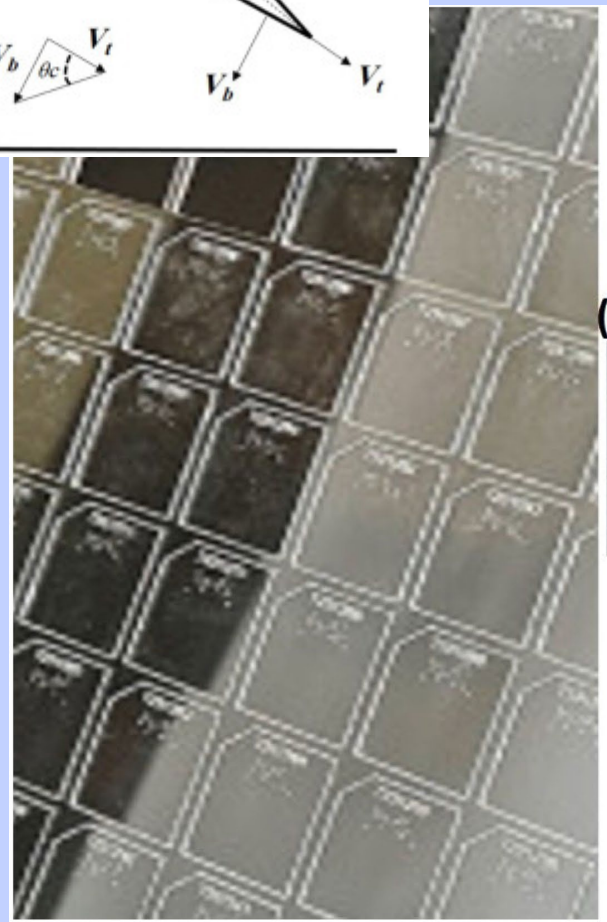
le particelle alfa emesse hanno energia di circa 5.5 MeV!
Un legame chimico C-C ha energia di circa 80 Kcal/mol
Fatte le dovute conversioni arriviamo a circa **3 eV per legame** → dunque lungo la traccia della particella alfa si verificano rotture di legami, anche dovute a elettroni secondari (raggi δ)

Le superfici di CR39 irraggiate con α presentano una struttura chimica severamente danneggiata

Lungo la traccia della particella α il processo di etching è più **VELOCE**



ma quanto è «profonda» la penetrazione della particella α?



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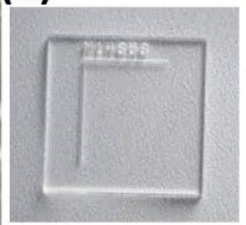
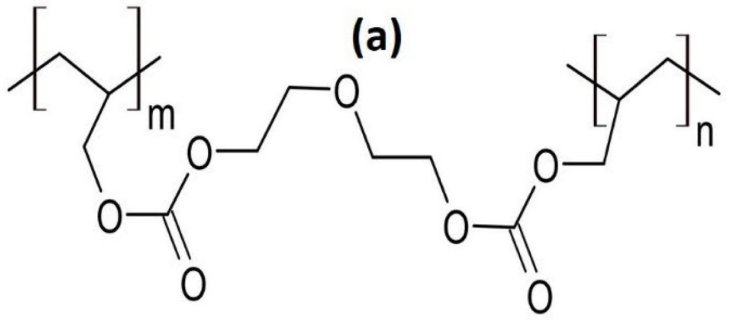
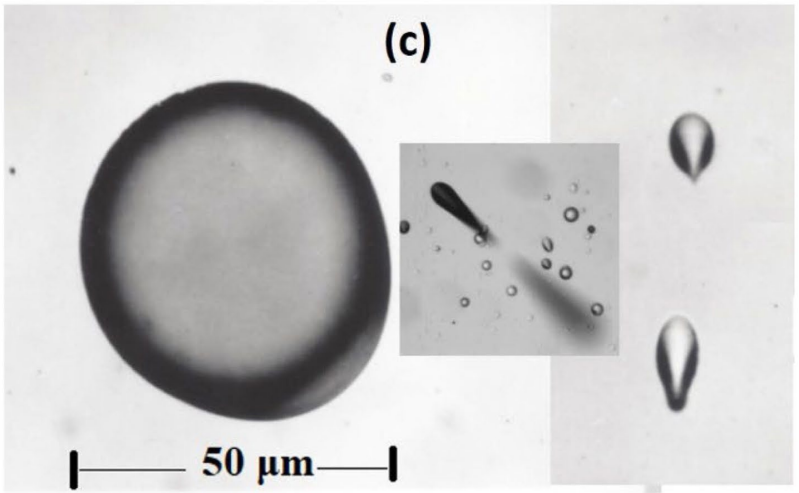
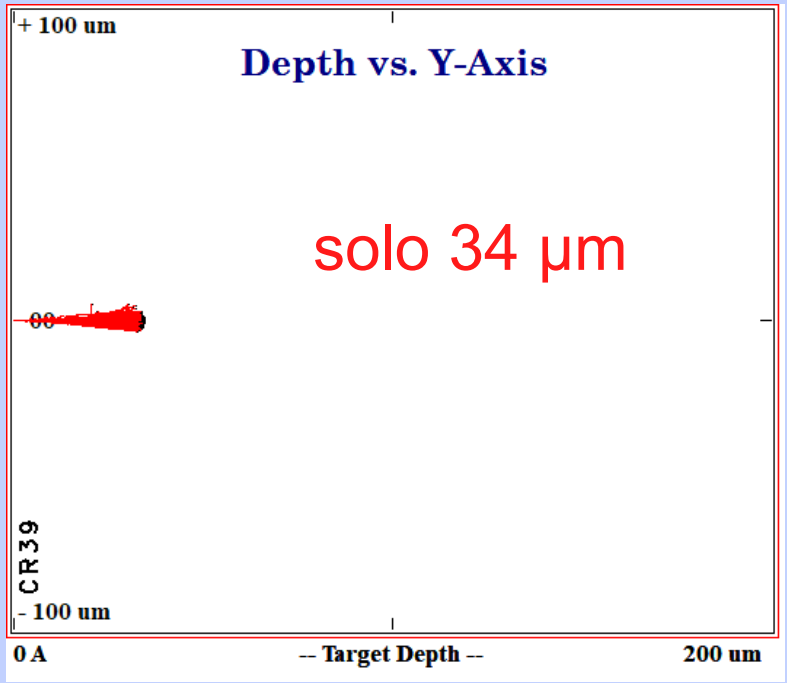


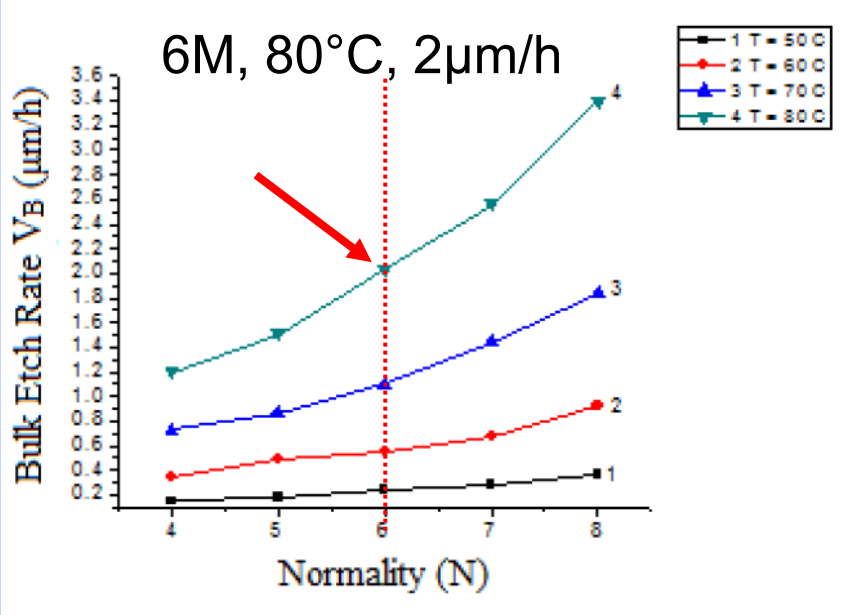




SRIM: the stopping and range of ions in matter



c'è da chiedersi, quanto deve durare il processo di etching per evidenziare le tracce delle particelle? Dipende da etch rate, c'è chi l'ha studiata, in varie condizioni di temperatura e concentrazione di NaOH



questa è la velocità di erosione del bulk, ovvero del CR 39 **non irraggiato**

la velocità di erosione della traccia lasciata dalla particella α è **quasi il doppio** nelle stesse condizioni!

quindi dopo 6h avrò eroso 12 µm di CR39 non irraggiato e più di 20 µm nel punto irraggiato→ 6h sono sufficienti a evidenziare le tracce!

Passiamo all’osservazione pratica…