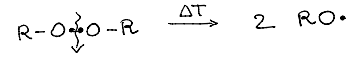
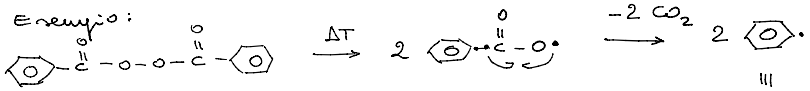
POLIMERI DI ADDIZIONE o A CRESCITA DI CATENA

MECCANISMO RADICALICO

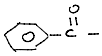
1. INIZIAZIONE



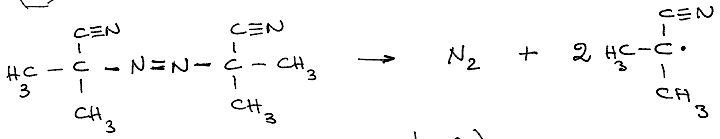
Esempio:



Perossido di BENZOILE



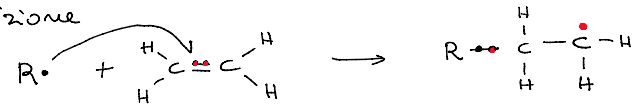
Benzoile



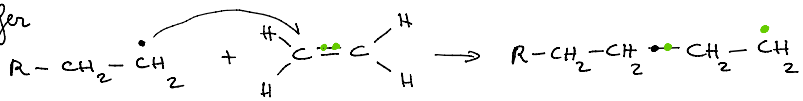
2,2'-Azobis (isobutirronitrile)

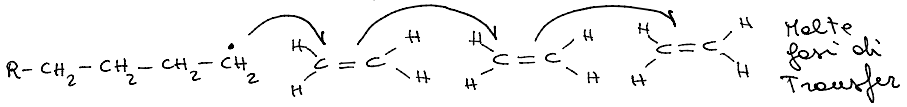
PROPAGAZIONE

Addizione

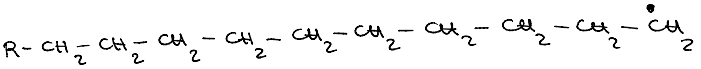


Transfer



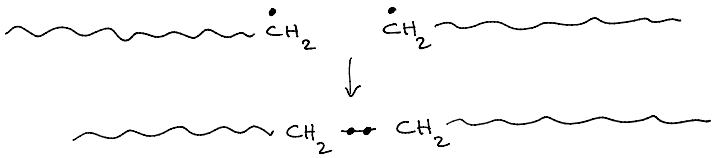


Molte fasi di Transfer

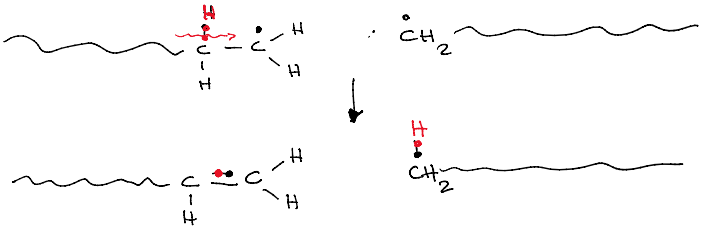


TERMINAZIONE

1. COMBINAZIONE

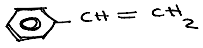


2. DISPROPORZIONE



Polimerizzazione radicalica del propilene

$CH_3-CH=CH_2$

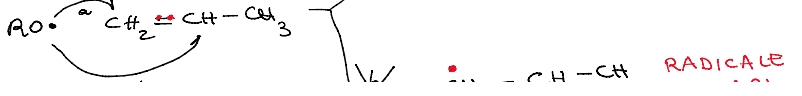


Stirene

Iniziazione $ROOR \xrightarrow{\Delta T} 2\,RO\bullet$

Propagazione

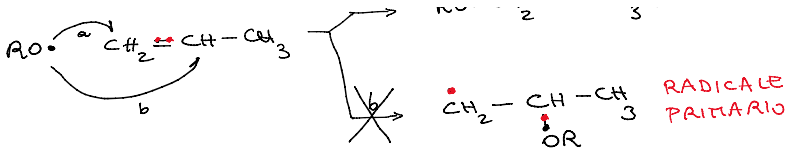
Addizione



RADICALE SECONDARIO

RADICALE

Propagazione Addizione



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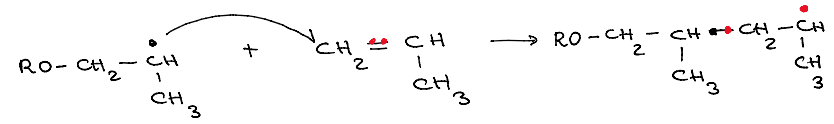
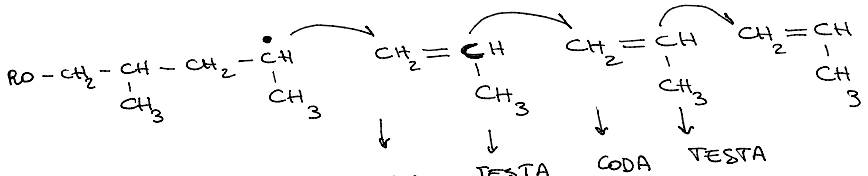
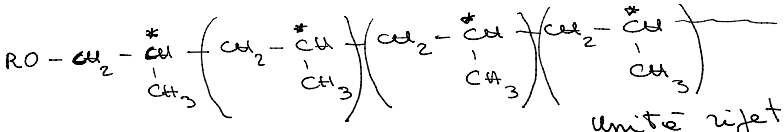
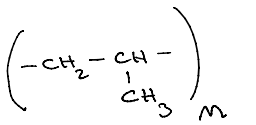




L'inserimento è ordinato e di tipo TESTA-CODA



unità ripetitive quello che "resta" dell'alchene dopo l'inserimento nella catena



polipropilene (PP)

nome del monomero

propil**ENE** → doppio legame

POLIMERI STEREOREGOLARI
- POLIMERI ISOTATTICI — Uguale configurazione di tutti i C* — R-R-R-R-R- / S-S-S-S-S-
- POLIMERI SINDIOTATTICI — Configurazioni alternate — R-S-R-S-R-S

POLIMERI ATATTICI — Distribuzione Random delle configurazioni — R-R-S-R-S-S-S-

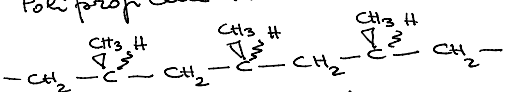
I polimeri stereoregolari hanno una temperatura di transizione vetrosa più alta di quelli atattici

Liquido

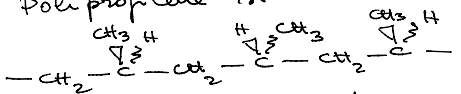
Solido Gommoso ↑ scalda ΔT

Solido Vetroso

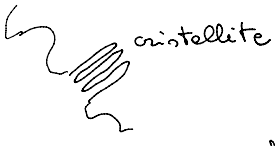
Polipropilene isotattico



Polipropilene sindiotattico



Polimeri stereoregolari hanno un certo grado di cristallinità (cristalliti)



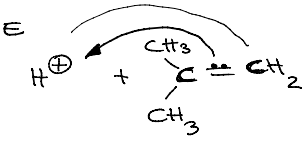
I polimeri stereoregolari si ottengono utilizzando particolari catalizzatori (ZIEGLER-NATTA $TiCl_4$ $Al(CH_2CH_3)_3$) meccanismo ionico di coordinazione.

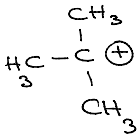
MECCANISMO CATIONICO

INIZIAZIONE
Come iniziatore si utilizza un acido protico (H_2SO_4) oppure un acido di Lewis (BF_3, $AlCl_3$)

$H^{\oplus}$

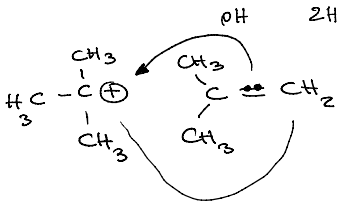
PROPAGAZIONE
Addizione

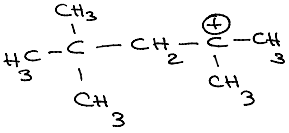


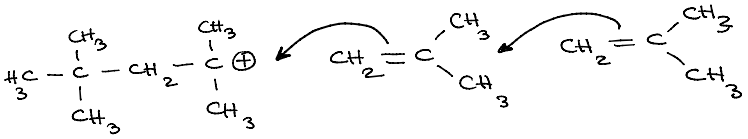


Carbocatione Terziario

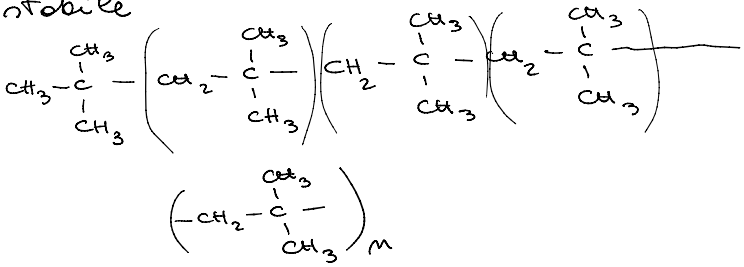
Transfer



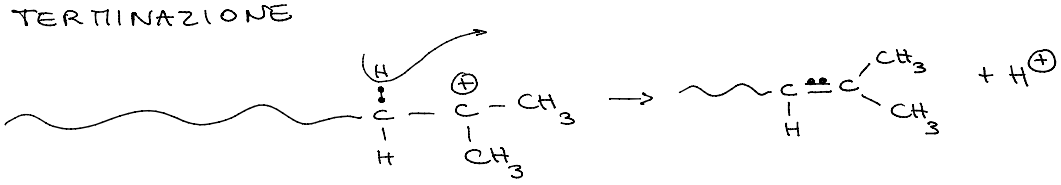


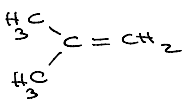
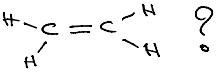


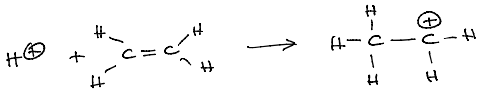
Inserimento ordinato TESTA-CODA che permette di formare il carbocatione più stabile



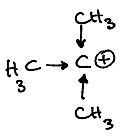
TERMINAZIONE



Perché ho scelto  e non  ?



Carbocatione primario
POCO STABILE



gruppi elettron donatori => per effetto induttivo "spingono" (riducono) la carica $\oplus$

Per il meccanismo cationico vanno bene alcheni con gruppi sostituenti elettron-donatori

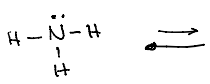
MECCANISMO ANIONICO

INIZIAZIONE
Come iniziatore si utilizzano BASI FORTI
($\ddot{N}H_2^{\ominus}$ o $CH_3CH_2CH_2CH_2Li$)

$\ddot{N}H_2^{\ominus}$ IONE AMMIDURO o AMMONIURO

BASE FORTISSIMA (più forte NaOH, KOH)

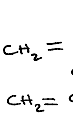
NH_2 AMMONIURO (più forte NaOH, KOH)



ACIDO DEBOLISSIMO

$K_a = 10^{-35}$

BASE CONIUGATA FORTISSIMA



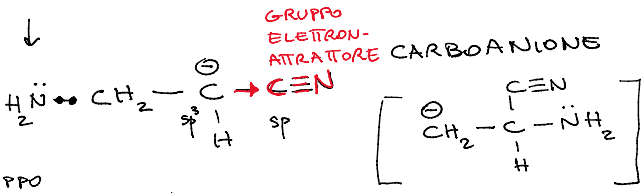
Acido ACRILICO

ACRILONITRILE Il nitrile (cianuro organico) dell'Acido Acrilico

PROPAGAZIONE

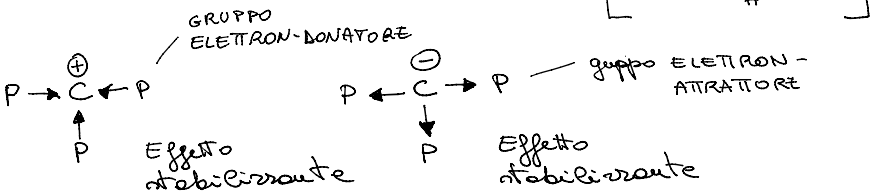
Addizione

ACRILONITRILE



GRUPPO ELETTRON-ATTRATTORE

CARBOANIONE

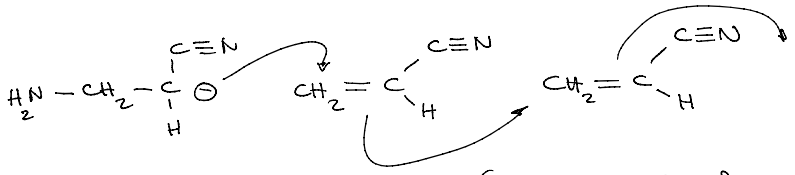


GRUPPO ELETTRON-DONATORE

Effetto stabilizzante

gruppo ELETTRON-ATTRATTORE

Effetto stabilizzante



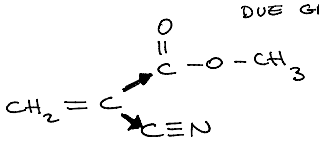
Inserimento TESTA-CODA (permette la formazione dell'anione più stabile)

TERMINAZIONE

Non esiste nella polimerizzazione anionica

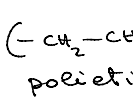
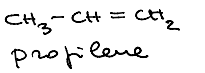
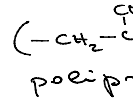
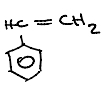
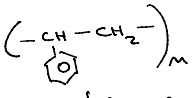
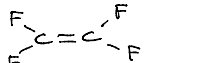
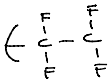
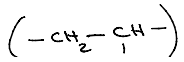
POLIMERI VIVENTI

DUE GRUPPI ELETTRON-ATTRATTORI ⇒ ANIONE PIÙ STABILE ⇒ HIGHER MONOMERO PER LA POL. ANIONICA

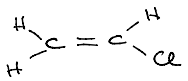


Super colle

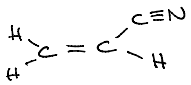
α-CIANO ACRILATO DI METILE

Monomero	Polimero
 etilene	 polietilene (PE)
 propilene	 polipropilene (PP)
 Stirene	 Polistirene (PS) Polistirolo
 Tetrafluoro etilene	 Politetrafluoroetilene TEFLON
	

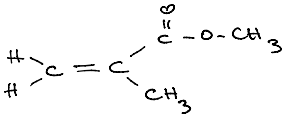
Tetrafluoro etilene



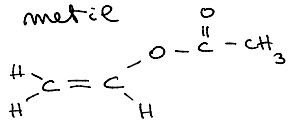
Cloruro di vinile



Acrilonitrile

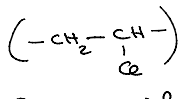


Metil Acrilato di metile

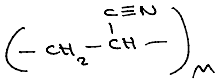


Acetato di vinile

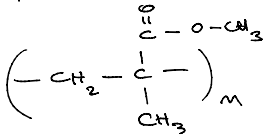
Politetrafluoro...



Poli vinil cloruro (PVC)

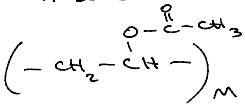


Poli acrilonitrile ORLON



PLEXIGLAS

Poli Metil Acrilato di Metile



Poli vinil acetato
Poli acetato di vinile