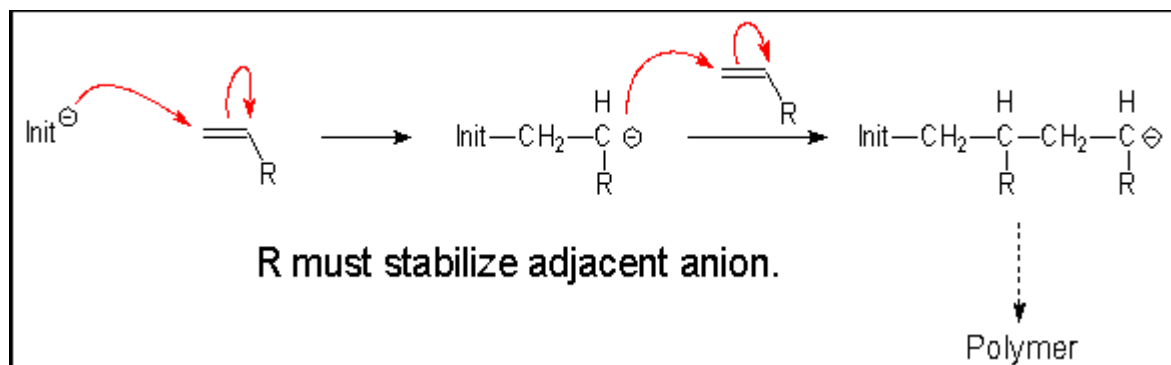


B.11) ANIÓNICAS VIVIENTES: QUÍMICA

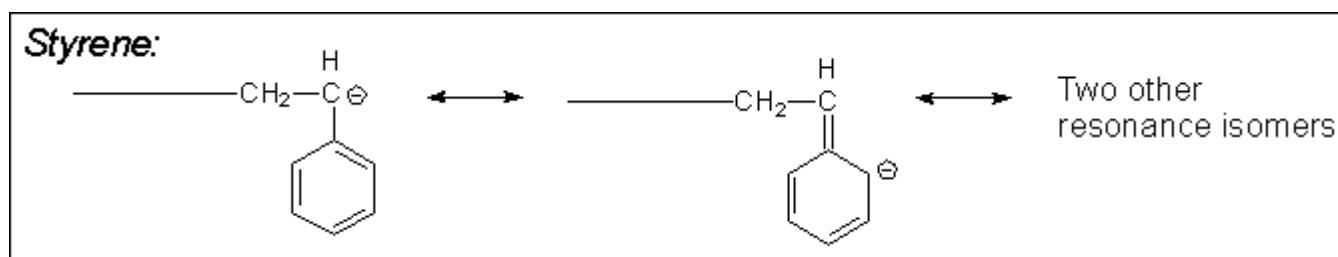
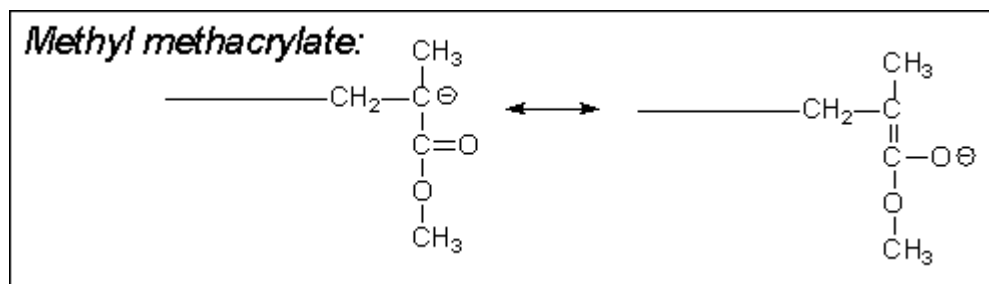
<http://chem.chem.rochester.edu/~chem421/anionic.htm>

The mechanism of anionic polymerization is a kind of repetitive conjugate addition reaction (the "Michael reaction" in organic chemistry).



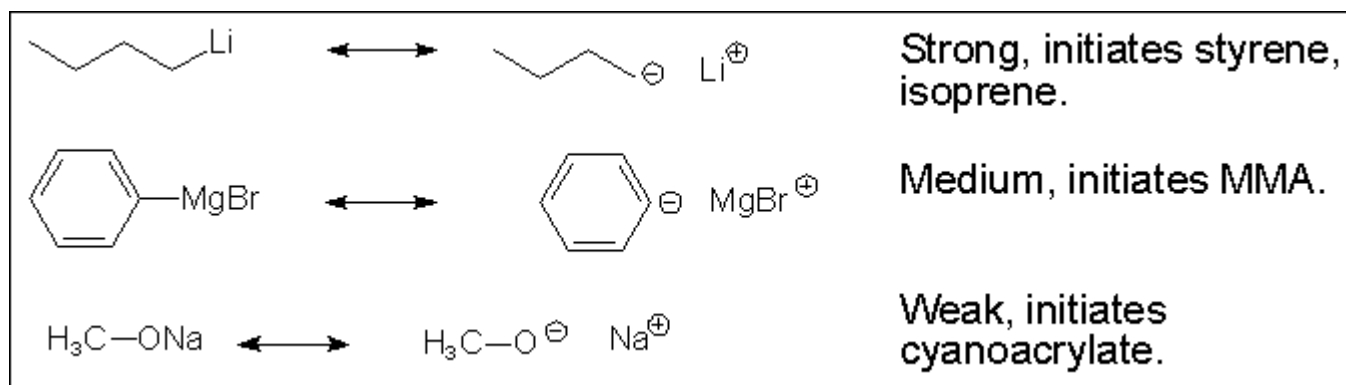
Electron withdrawing groups (ester, cyano) or groups with double bonds (phenyl, vinyl) are needed as the R groups because these can stabilize the propagating species by resonance.

Examples:

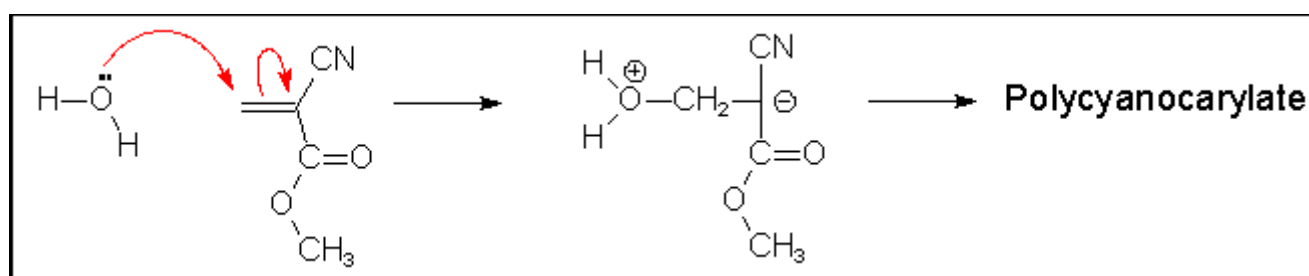


Anionic Initiation

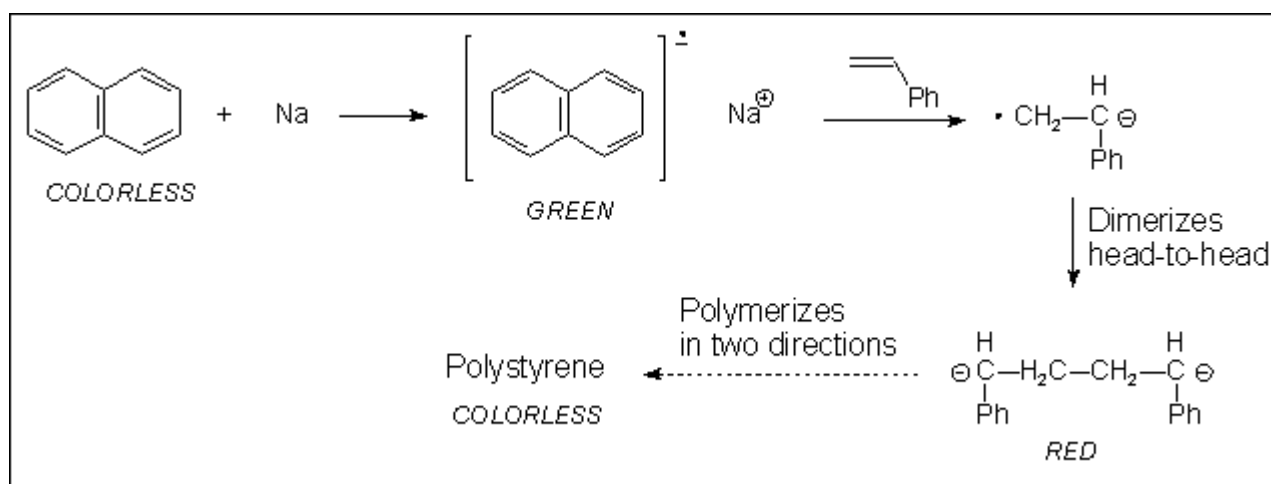
For initiation to be successful, the free energy of the initiation step must be favorable. Therefore, it is necessary to match the monomer with the appropriate strength of initiator so that the first addition is "downhill." If the propagating anion is not very strongly stabilized, a powerful nucleophile is required as initiator. On the other hand, if the propagating anion is strongly stabilized, a rather weak nucleophile will be successful as initiator. (Of course, more powerful ones would work, too, in the latter case.)



But two EWGs are so effective in stabilizing anions that even water can initiate cyanoacrylate ("Super Glue"). Weak bases (such as those on the proteins in skin) work even better.



There is one other category of initiator, known as *electron transfer*, that works best with styrene and related monomers. The actual initiating species is derived from an alkali metal like sodium. An aromatic compound is required to catalyze the process by accepting an electron from sodium to form a radical anion salt with Na^+ counterion. A polar solvent is required to stabilize this complex salt. The electron is subsequently transferred to the monomer to create a new radical anion which quickly dimerizes by free radical combination (similar to the termination reaction in free radical polymerization). The eventual result is a *dianion*, with reactive groups at either end. Propagation then occurs from the middle outwards. This system is especially useful for producing ABA block copolymers, which have important technological uses as thermoplastic elastomers.



Effects of Conditions on Reaction Rates

Because the propagating species carries a counterion, the "tightness" of the ion pair is strongly affected by the reaction conditions. The tighter the ion pair, the slower the rate of propagation.

This feature is apparent in the following comparison of rates for an anionic polymerization in solvents of increasing polarity:

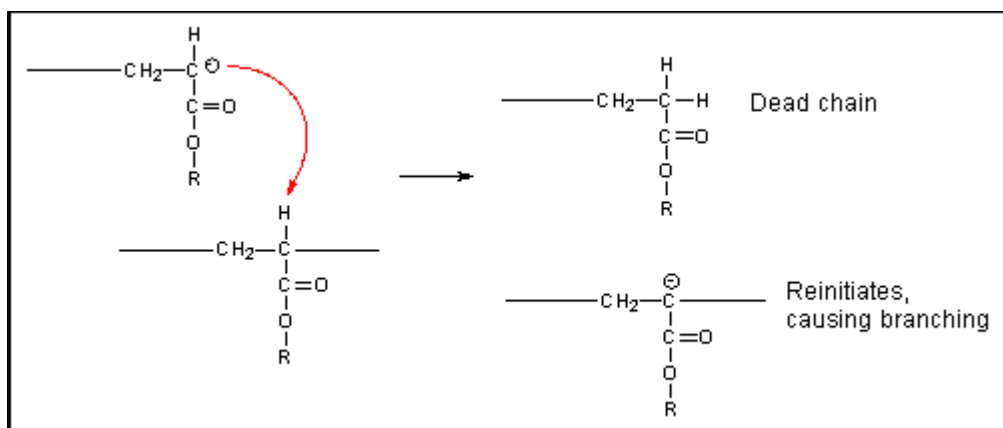
| Solvent | Relative Rate |
|---------------------|---------------|
| Benzene | 1 |
| Dioxane | 2.5 |
| THF | 225 |
| 1,2-Dimethoxyethane | 1900 |

Similarly, larger counterions usually form looser ion pairs, so there is an increase in rate as you go down the periodic table:

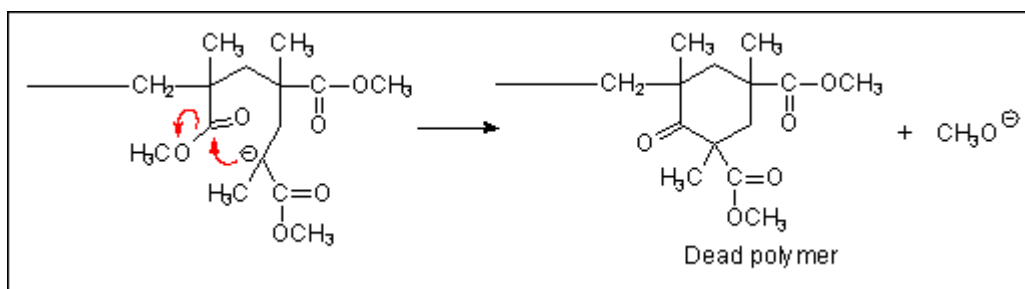
| Counterion | Relative Rate |
|-----------------|---------------|
| Li ⁺ | 1 |
| Na ⁺ | 3.6 |
| K ⁺ | 21.1 |
| Rb ⁺ | 22.9 |
| Cs ⁺ | 26.1 |

Undesirable Side Reactions

Acrylates have problems in anionic propagation because of chain transfer to polymer. The hydrogen atoms adjacent to the ester groups are slightly acidic, and can be pulled off by the propagating anion. The new anion thus created can reinitiate, leading to branched polymers. This side reaction is difficult to suppress (see papers in the literature by P. Teyssie).



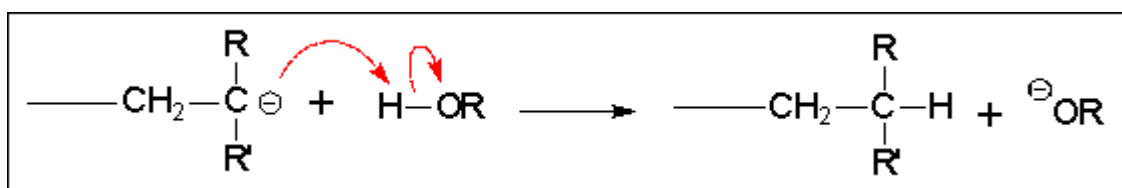
Methacrylates have a methyl group instead of the hydrogen, so the above reaction is not a problem. However, both acrylates and methacrylates suffer from potential reactions at the ester instead of the vinyl group (called the "Claisen condensation" in organic chemistry). The most common circumstance is reaction with the ester two repeat units back, because the transition state is a six-membered ring (entropically favorable). The reaction causes a cyclization, and ejects an alkoxide as a leaving group. Alkoxide is too weak of a nucleophile to reinitiate, so this process is a termination. The reaction can also occur further back in the same chain, or in the middle of a separate chain, but the chemistry depicted predominates.



If polymerized anionically and allowed to stand, the end groups of PMMA are all the rings shown above. However, the polymerization can still be accomplished because of a stroke of luck. The activation energy of cyclization is greater than that of propagation, so the former is affected more by temperature than the latter. Simply by running the reaction at low temperatures, the undesired cyclization reaction is suppressed, and propagation occurs without problem. (The low temperature decreases the rate of both the cyclization and propagation reactions, but decreases the rate of cyclization more.) Unfortunately, cooling large reactors is inefficient and costly, so anionic polymerization of methacrylates is not practiced commercially despite the desirable characteristics of the polymers produced. Group transfer polymerization provides a partial solution to this problem. (See Young & Lovell Ch 2.13.)

Termination

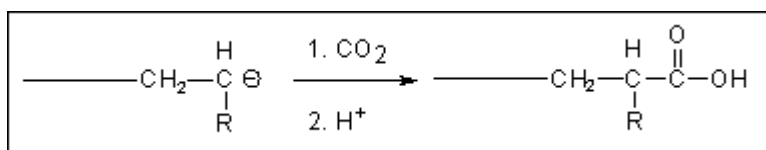
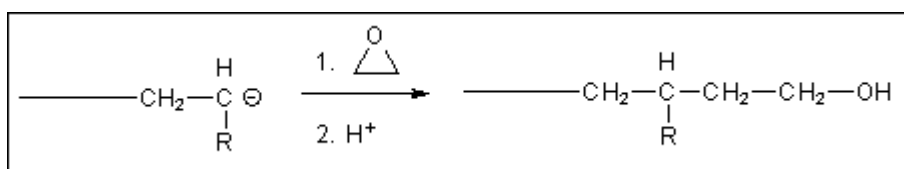
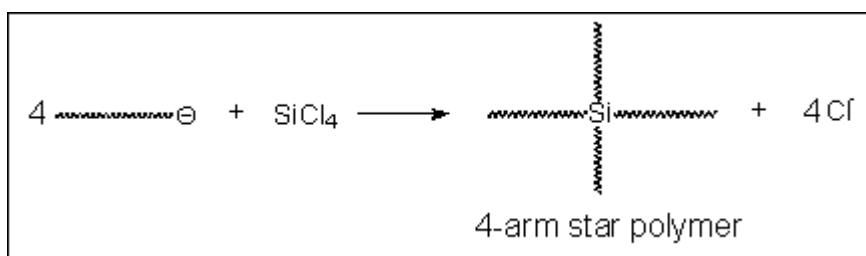
When carried out under the appropriate conditions, *termination reactions do not occur in anionic polymerization*. One usually adds purposefully a compound such as water or alcohol to terminate the process. The new anionic species is too weak to reinitiate.



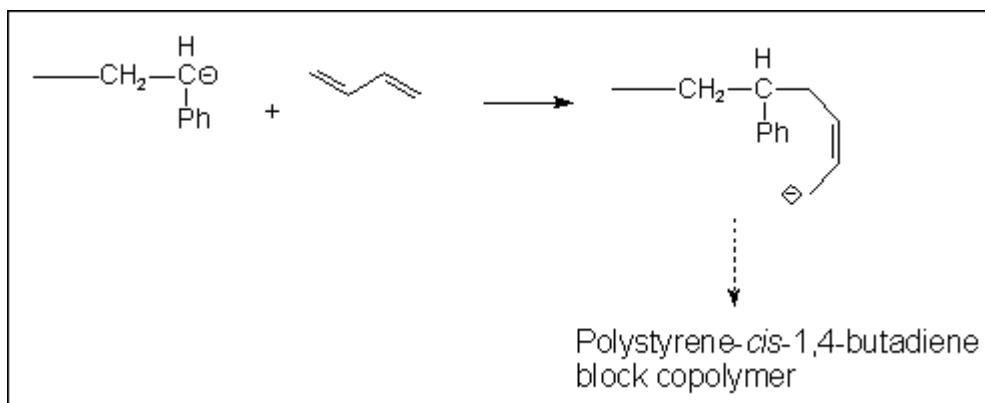
The "Dark Side:" Compounds such as water, alcohols, molecular oxygen, carbon dioxide, etc. react very quickly with the carbanions at the chain ends, terminating the propagation. Therefore, one must scrupulously dry and deaerate the polymerization ingredients to be able to get a truly living system. This is not easy to do, and adds to the potential costs of the process.

Functionalization of the Chain Ends

The beauty of anionic polymerization lies in the lack of termination reactions when carried out under the appropriate conditions (*living polymerization*). This means that the propagating species remains unchanged at the chain end when the monomer is consumed, so subsequent chemical reactions can be carried out. (The chain end is a carbanion, and the organic chemistry of carbanions is diverse.) Here are a few examples among many possible:

Carboxylation of end groups:**Alcohol end groups via ethylene oxide:****Coupling agents:****Block Copolymerization**

If the chain ends remain reactive when the monomer is consumed, one could add more monomer and continue the reaction. Of course, one does not have to add the same monomer again. Switching over to another monomer leads to propagation of a new chain covalently bound to the previous one (*block copolymer*), as in the following example for styrene and butadiene:



Living polymerization is required for successful synthesis of block copolymers.

Block copolymers have important technological uses because they often exhibit *hybrid* rather than *average* properties.. For example, if one block is hydrophilic but the other hydrophobic, the result is a surfactant. In fact, the strongest known surfactants are made this way.

Another application requires one or more blocks of flexible, low T_g polymer, with other blocks of rigid, high T_g polymer. The hard and soft blocks segregate in the solid state, and the polymer actually exhibits *two glass transitions*, one at high temperature and a second one below room temperature. The resulting material behaves like a filled rubber, with the important distinction that the hard domains can be melted at elevated temperature (above their T_g). This means that, unlike conventional rubbers that are covalently crosslinked (*vulcanized*), these block copolymers (known as *thermoplastic elastomers*) can be processed thermally and molded. The crosslinking in the block copolymers is physical, due to entanglements of the chains in the hard domains. Conventional rubbers are thermosets, and must be crosslinked in the mold. They cannot be remelted without decomposition.

Commercial examples are the ABA triblock copolymers (where A = styrene and B = 1,4-butadiene, isoprene, or hydrogenated versions of these), thermoplastic elastomers sold by Shell as "Kraton" and widely used as shoe sole material. Other examples, although not made by anionic polymerization, are the Spandex fibers (e.g., Lycra) which are actually *multiblock* copolymers with hard and soft segments.