FREE-RADICAL VERSUS ANIONIC POLYMERIZATION

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| ANIONIC (LIVING) POLYMERIZATION VERSUS FREE-RADICAL POLYMERIZATION | |
| **Anionic Polymerization** | **Free-Radical Polymerization** |
| There is no termination step unless contaminations such as water or alcohol are present or deliberately added to terminate the reactions. | Chain growth termination occurs via combination or disproportionation which compete with chain growth and chain transfer reactions. |
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| The initiation of anionic polymerization has typically a much smaller activation energy than the corresponding free-radical polymerization. | Free-radical polymerizations require potent initiators (and coinitiators). The rate constant for initiator dissociation is much smaller than that for propagation. |
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| Anionic polymerization reactions are rather insensitive to temperature and can be carried out at very low temperatures but are only suitable for monomers with strong electron withdrawing groups. | Initiation and propagation are strongly affected by the reaction temperature. An increase in temperature almost always increases the rate of chain propagation but it also increases chain transferand thus lowering the molecular weight. |
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| Anionic polymerization reactions yield more regular polymers with less branching, more controlled tacticity and narrow molecular weight distribution. | The degree of polymerization depends on the velocity constants of radical formation, chain growth, chain transfer and chain termination. |
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| Anionic polymerizations are difficult to carry out and are only used on an industrial scale if the monomer in question does not polymerize by free-radical mechanism or when polymers with regular structure are required. It is often the method of choice for the synthesis of well defined block copolymers. | Free-radical polymerization is the most versatile type of chain-growth polymerization. Because of the non-specific nature of the free radicals towards vinyl monomers, many monomers can be copolymerized. However, well defined block copolymers are difficult to make and the MWD is broader. |