IONIC POLYMERIZATION
(Addition or Chain-growth)

At the end of this lecture, you should be able to:

- Understand what is the difference between free-radical and ionic polymerization.
- Understand the types of ionic polymerization (cationic and anionic polymerization).
- Understand the kinetic of ionic polymerization.
- Understand what is meant by ”living polymer”.

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- Chain-reaction polymerization is known to occur by several mechanisms other than those involving free radicals as in the discussed in the previous lectures. Prominent among these are reactions in which the chain carriers are ***carbenium** ions (cationic polymerization,)* or **carbanions** *(anionic polymerization)* .

- Accordingly, ionic polymerization is a chain-growth polymerization in which active centers are ions. It can be considered as an alternative to radical polymerization, and may refer to anionic polymerization or cationic polymerization.

- In addition, polymerization may take place by mechanisms involving coordination compounds among the monomer, the growing chain, and a catalyst, usually a solid *(coordination or insertion polymerization)*.

- The mechanisms of' these polymerizations are less thoroughly understood than that of radical polymerization, for several reasons. (1) Reaction systems are often heterogeneous, involving inorganic catalysts and organic monomers (2) Usually large effects may be produced by a third component *(cocatalyst)* present in very low concentration. (3) Polymerization often leads to very-high-molecular-weight polymer at an extremely high rate, increasing enormously the difficulty in obtaining kinetic data or even reproducible results

Monomer Type	Polymerization Mechanism[b]			
	Radical	Cationic	Anionic	Coordination
Ethylene	+	+	−	+
Propylene and α-olefins	−	−	−	+
Isobutylene	−	+	−	−
Dienes	+	−	+	+
Styrene	+	+	+	+
Vinyl chloride	+	−	−	+
Vinylidene chloride	+	−	+	−
Vinyl fluoride	+	−	−	−
Tetrafluoroethylene	+	−	−	+
Vinyl ethers	−	+	−	+
Vinyl esters	+	−	−	−
Acrylic and methacrylic esters	+	−	+	+
Acrylonitrile	+	−	+	+

[a] Lenz (1967).

[b] + = high polymer formed; − = no reaction or oligomers only.

Cationic polymerization

Typical catalysts for cationic polymerization include, in order of importance, a protonic acids (Lewis acids and Friedel-Crafts halides), protonic (Bronsted) acids, and stable carbenium-ion salts. All these are strong electron acceptors. Many of them, particularly the Lewis acids, require a cocatalyst, usually a Lewis base to initiate polymerization. So, monomers with electron-donating (that can form stable carbenium ions) are polymerized by cationic mechanisms.

Characteristics of Cationic Polymerization

1. High rate of polymerization at low temperatures is a characteristic of cationic polymerizations.
2. It is often difficult to establish uniform reaction conditions before the reactants are consumed.
3. The polymerization of isobutylene by $AlCl_3$, or BF_3, takes place within a few seconds at – 100 ^{o}C, producing polymer of molecular weight up to several million.
4. Both rate and molecular weight are much lower at room temperature. These considerations limit the industrial application of cationic polymerization to the above-mentioned example.

Kinetic of Cationic polymerization

Although many cationic polymerizations proceed so rapidly that it is difficult to establish the steady state, the following kinetic scheme appears to be valid.

Let the catalyst be designated by A and the cocatalyst by RH. Initiation, propagation, termination, and transfer may be represented as follows:

$$\mathrm{A} + \mathrm{RH} \overset{K}{\rightleftharpoons} \mathrm{H}^{+-}\mathrm{AR}$$

$$\mathrm{H}^{+-}\mathrm{AR} + \mathrm{M} \xrightarrow{k_i} \mathrm{HM}^{+-}\mathrm{AR} \quad \Big\} \ \textit{Initiation}$$

$$\mathrm{HM}_x{}^{+-}\mathrm{AR} + \mathrm{M} \xrightarrow{k_p} \mathrm{HM}_{x+1}{}^{+-}\mathrm{AR} \quad \Big\} \ \textit{Propagation}$$

$$\mathrm{HM}_x{}^{+-}\mathrm{AR} \xrightarrow{k_t} \mathrm{M}_x + \mathrm{H}^{+-}\mathrm{AR} \quad \Big\} \ \textit{Termination}$$

$$\mathrm{HM}_x{}^{+-}\mathrm{AR} + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_x + \mathrm{HM}^{+-}\mathrm{AR} \quad \Big\} \ \textit{Chain-Transfer}$$

The rate of initiation is

$$R_i = Kk_i[\mathrm{A}][\mathrm{RH}][\mathrm{M}]$$

Since, in strong contrast to radical polymerization, termination is first order,

$$R_t = k_t[\mathrm{M}^+]$$

where $[\mathrm{M}^+]$ is written as an abbreviation for [HM+-AR]. By the steady-state assumption (which appears to hold in most cases, despite uncertainty as to whether such a state is actually achieved),

$$[\mathrm{M}^+] = \frac{Kk_i}{k_t}[\mathrm{A}][\mathrm{RH}][\mathrm{M}]$$

The overall polymerization rate is

$$R_p = k_p[\mathrm{M}][\mathrm{M}^+] = K\frac{k_ik_p}{k_t}[\mathrm{A}][\mathrm{RH}][\mathrm{M}]^2$$

Assume that the termination predominates over transfer,

$$\bar{x}_n = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}^+][\mathrm{M}]}{k_t[\mathrm{M}^+]} = \frac{k_p}{k_t}[\mathrm{M}]$$

Kinetic of Anionic polymerization

Anionic polymerization was carried out on a commercial scale for many years before the nature of' the polymerization was recognized, in the production of' the buna-type synthetic rubbers in Germany and Russia by the polymerization of' butadiene with sodium or potassium amide as the catalyst. The first anionic chain reaction to be so identified was the polymerization of' methacrylonitrile by sodium in *liquid ammonia* at -75 ^{o}C. In modern times, the growth of' commercial products of' anionic polymerization has been phenomenal (Hsieh 1981). Most of' these polymerizations are based on the use of *organometal catalyst* systems, which allow unprecedented control over polymer structure. In addition to the monomer types listed in Table 1, monomers that be polymerized by ring scission may do so by anionic mechanisms..

The kinetics of anionic polymerization may be illustrated by the polymerization of' styrene with potassium amide in liquid ammonia:

$$KNH_2 \xrightarrow{K} K^+ + NH_2^-$$

$$NH_2^- + M \xrightarrow{k_i} NH_2M^- \quad \text{Initiation}$$

$$NH_2M_x^- + M \xrightarrow{k_p} NH_2M_{x+1}^- \quad \text{Propagation}$$

$$NH_2M_x^- + NH_3 \xrightarrow{k_{tr}} NH_2M_xH + NH_2^- \quad \text{Chain-Transfer}$$

Living Polymer

NOTE: termination step can be done by adding a terminator agent like Water.

Similar to other mechanisms (i.e. at steady- state conditions) the usual kinetic analysis leads to an equation for degree of' polymerization as follows:

$$R_p = \frac{Kk_pk_i}{k_{tr}}\frac{[NH_2^-]}{[NH_3]}[M]^2$$

and

$$\bar{x}_n = \frac{k_p[M]}{k_{tr}[NH_3]}$$

"Living" Polymers

Living polymers are polymers that retain their ability to propagate and grow to a desired size while their degree of termination or chain transfer is still negligible.

Since the termination step usually involves transfer to some species not essential to the reaction, anionic polymerization with carefully purified reagents may lead to systems in which termination is lacking. The resulting species, called "living" polymers can be prepared, for example, by polymerizing styrene with sodium naphthalene. Kinetic analysis shows that the polymer can have an extremely narrow distribution of' molecular weight and for all practical purposes be essentially monodisperse; if initiation is rapid compared to propagation. The polymer can be "killed" by addition of' a terminating agent, for example, water, at the end of the reaction The living polymer technique provides an unique opportunity for the preparation of block copolymers of' precisely defined composition.

HIGHLIGHT

Living Polymers. Their Discovery, Characterization, and Properties.

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Dr. Szwarc received his Ph.D. and Dsc degrees from Manchester University, England (in 1947 and 1949, respectively) where he served as lecturer and continued his research on determination of Bond Dissociation Energies of polyatomic molecules until 1952. During that time he discovered the then unknown quinonoid hydrocarbon, $CH_2{=}C_6H_4{=}CH_2$ and its spontaneous polymerization. This led to his interest in Polymer Chemistry and to his appointment in 1952 as a Professor of Physical and Polymer Chemistry of the New York State College of Environmental Science and Forestry in Syracuse, New York. Eventually he organized a New York State Polymer Center, serving as its director until his retirement in 1979 when he moved to San Diego, California.

M. Szwarc

HONORS AND AWARDS

Elected to the Royal Society, London in 1966; Appointed by the Royal Swedish Academy of Science as Nobel Guest Professor (1968–1972); Baker Lecturer at Cornell University (1972); Lemieux Lecturer at University of Ottawa (1976); Elected to the Polish Academy of Sciences, 1988; Recipient of American Chemical Society Award, 1969; International Plastic and Engineering Society Award, 1972; Gold Medal of Benjamin Franklin Society, 1978; Herman Mark Award, 1990; Kyoto Award, 1991.

HONORARY DOCTORATE DEGREES

Leuven University, Belgium, 1975
Uppsala University, Sweden, 1975
Louis Pasteur University, Strasbourg, France, 1978

Author of about 500 scientific papers and reviews, of three books and editor of two volumes of "Ions and Ion-Pairs in Organic Chemistry."

USEFUL LINK:
https://www.youtube.com/watch?v=9vD8tfSMEVk&t=194s

THANK YOU FOR LISTENING