

Polymers, both natural and synthetic, are omnipresent in our everyday life. Pipes that deliver water to our homes, bags to carry the goods we purchase, tires and many other parts of our cars, textiles that make our clothes, casings of our electronic devices, paints and coatings, wire shielding in cables, are only a few examples. Polymers are also commonly used in medicine, as sutures, syringes, wound dressings, drug components as well as modern drug- and gene-delivery systems. Natural polymers – proteins, polysaccharides and nucleic acids – are the basic components of living organisms. Therefore, precise understanding of chemical reactions of polymers is of great scientific and practical importance.

Polymers can be depicted as long (often very long) molecules consisting of many repeating units. Most polymer chains are flexible. In solid polymers these chains are stacked together either in a random, chaotic manner in the so-called amorphous phase or ordered in a way that some chain fragments are parallel to each other forming regular patterns (crystalline phase). While the presence of crystalline phase makes the polymer more mechanically resistant, it is still composed of independent polymer chains that are not strongly and permanently linked together. However, if we manage to link the polymer chains together by “unbreakable”, permanent chemical bonds, we form a three-dimensional network of polymer chains and the resulting material has very different (typically much better) properties when compared to a material where polymer chains are not linked to each other. Cross-linked polymers have much better mechanical properties, high resistance to solvents, better thermal properties, etc. Moreover, they can be used to form interesting and valuable materials, including hydrogels. The latter, made of cross-linked hydrophilic polymers, can swell in water to an equilibrium and resemble gelatin jelly, but are much stronger. They are applied, for instance, as transparent wound dressings. Their special forms, so-called intelligent gels, can react by swelling and deswelling to external stimuli as pH, temperature, light, electric field, etc. Such hydrogels are very important for constructing systems for controlled delivery of drugs. In some cases, such products should be very small, in order to fit to the diameter of small capillary vessels in our cardiovascular system. In such case we speak of microgels and nanogels. Actually, the latter can be obtained by internal cross-linking of a single linear polymer chain. Such a chain in solution often attains a form of a loose coil. Now if we chemically clamp together some segments of such a coil, we obtain a spherical, loose molecular cage that can be used for delivering drugs, DNA fragments or radioisotopes to selected tissues of our bodies, as a form of targeted therapy. Often the hydrophilic polymers used to obtain such systems are polyelectrolytes, i.e. they bear positive or negative charge along their chains, to control their interactions with the carried drugs and with the target tissues.

In this project we will study cross-linking reactions in exemplary polyelectrolytes in aqueous solutions, focusing both on “regular” cross-linking between polymer chains and on internal (“intramolecular”) cross-linking between segments of the same polymer chain. In order to better understand how these reactions take place (i.e., to understand their mechanism), we will study how fast these reactions run (i.e., study their kinetics), for polymer chains of various length, and at various reaction conditions. This is a non-trivial task. Rates of chemical reactions are typically described by models developed for small molecules. We will have to use more complex, non-classical models, because our reactions occur between long molecules and their segments. Since most of these reactions are very fast, we will be initiating them in a very short time (nanoseconds to microseconds), by creating active sites – radicals – along polymer chains using very short pulses of ionizing radiation. Once these radicals are formed, we will follow their reactions, leading mainly to cross-linking. For this purpose we will use very fast, unique detection setups allowing to see, in real time, changes in the optical properties of polymer solutions, using spectrophotometry (since the radicals absorb light) and light scattering (since the polymers scatter light in a way that depends on their weight and size, both of which change during cross-linking).

The obtained kinetic results will allow to deepen our understanding of cross-linking reactions in polymer solutions. The gained knowledge can be applied in future to precisely design and synthesize more advanced cross-linked polymer structures, also in the nanoscale, for use in advanced medicine and technology.