

RADIATION-INDUCED SYNTHESIS OF POLYMERIC NANOGELS

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Introduction

The continuous need for new polymeric entities for biomedical application calls for a careful investigation of some dimensional aspects and topological features of polymers. In this context, several methodologies have been reported for the synthesis of nanogels. According to Encyclopedia of Nanotechnology [1] definition of these polymeric nanoparticles may be directly derived from definition of polymeric gel, i.e., a two-component system consisting of a permanent three-dimensional network of linked polymer chains, and molecules of a solvent filling the pores of this network. Based on this approach polymeric nanogels are classified as particles of polymer gels with colloidal properties, having the dimensions in the order of nanometers. One can also distinguish bigger analogues of micrometer size called respectively microgels. Another way of defining polymeric nano- and microgels is based on the specific form of these particles: all the chain segments are linked together, thus being a part of one macromolecule. That is why nano- and microgels as internally cross-linked polymeric chains are considered as a distinct type of macromolecules [2].

Results and Discussion

A number of synthetic routes have been developed for synthesis of nano- or microgels of different chemical structure, architecture and properties. These methods can be divided into two groups. The first one encompasses the techniques based on simultaneous polymerization and cross-linking (sometimes called cross-linking polymerization), where the substrates are monomers or their mixtures. The second group includes methods based on cross-linking of macromolecules where the starting material is not a monomer but a polymer. Works of Burchard and co-workers [3] give examples of microgel synthesis based on intramolecular cross-linking of polymeric chains. It has been shown that reaction of intramolecular cross-linking can be carried out with water-soluble polymers in dilute solutions (polymer concentration must be low enough to avoid intermolecular cross-linking) using a cross-linker capable of reacting with the chains functional groups (e.g.: -OH, -COOH or other). The weight and dimensions of the final product depend on the linear polymer chain weight and the cross-linker concentration which influences the internal cross-link density.

An alternative method of intramolecular cross-linking initiation is the use of ionizing radiation as proposed by Rosiak and coworkers [4,5]. Its undoubted advantage is the fact of avoiding any additives as the reaction can be performed in a pure polymer-solvent system. This method is particularly well suited for the preparation of products for biomedical applications.

When a polymer is subjected to ionizing radiation (typically gamma rays or high-energy electrons) in a dilute aqueous solution, most of the radiation energy is absorbed by water. As a result, short-lived reactive species, namely OH radicals, H-atoms and hydrated

electrons, are formed. The initial radiation chemical yields of these species in Ar-saturated solutions are $G(\text{OH}) = 2.8 \times 10^{-7} \text{ mol J}^{-1}$, $G(\text{H}) = 0.6 \times 10^{-7} \text{ mol J}^{-1}$, and $G(e_{\text{aq}}^-) = 2.7 \times 10^{-7} \text{ mol J}^{-1}$. Since electrons are inert towards simple, aliphatic water-soluble polymers, they can be converted into additional OH radicals by saturating the solution with N_2O . Hydroxyl radicals and hydrogen atoms are capable of abstracting hydrogen atoms from macromolecules, generating polymer radicals.

Macroradicals generated during irradiation of dilute aqueous polymer solution react in a number of different one-radical (chain scission, hydrogen transfer) and two-radical (cross-linking and disproportionation) reactions. Recombination may occur either between two radicals localized on separate macromolecules or between two radicals within the same chain. The proportion between recombination and disproportionation reactions is set by the radical structure and the possibility to control this parameter is usually very limited.

The basic reaction for the formation of nanogels upon irradiation of a polymer in solution is intramolecular cross-linking of polymer radicals. Since there is always a competition between this process and other reactions, the basic aim in the design of a synthetic procedure is to choose such conditions that promote intramolecular cross-linking and reduce the yield of the unwanted side processes, especially degradation and intermolecular cross-linking.

It has been shown that one of the most important factors in such case is the average number of radicals present simultaneously on each polymer chain. High numbers of radicals can be generated as a result of short but intense pulses of fast electrons. Detailed discussions on this topic have been given by Rosiak and his group [4-7]. If the average number of radicals per chain is lower than one, the single radical that does not find a reaction partner within its own macromolecule, can undergo scission or rearrangements that may change its nature and life-time or can recombine with a radical on a neighboring polymer chain. As a result of that, the macromolecules become linked together, the average molecular weight increases and, finally, a macroscopic, "wall-to-wall" hydrogel is formed. On the other hand, when the number of radicals per chain significantly exceeds one, intramolecular cross-linking dominates, leading to the formation of nanogels. Such reaction conditions can be achieved by lowering the polymer concentration and increasing the dose per electron pulse.

In this work summary on radiation induced intramolecular crosslinking will be given including information on parameters influencing synthesis of nanogels, mechanism and kinetics of this process, physico-chemical properties of irradiation products as well as preliminary application attempts.

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