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Mendeleev Commun., 2019, **29**, 589–591

Mendeleev Communications

Self-disassembly of plant macromolecules

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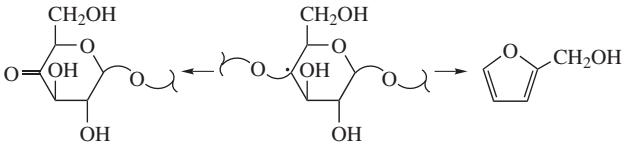
DOI: 10.1016/j.mencom.2019.09.038

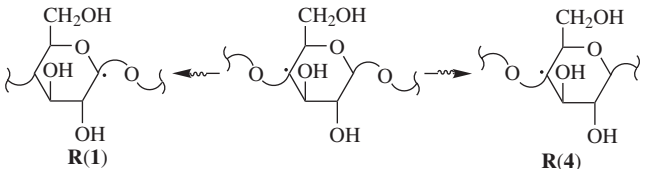
Plant macromolecules can be decomposed *via* a self-disassembly mechanism consisting in the sequential removal of monocyclic fragments from the end of the macromolecule. The radiolytically initiated process is supported by moderate heating. Self-disassembly programs are encoded in the structure of the radical centers.



According to early studies,[1–3] ionizing radiation causes a random cleavage of bonds between monomer units in polysaccharides and polyphenols, giving shorter solid oligomers. Thus, plant macromolecules undergo partial depolymerization. The mechanism of this process was discovered and detailed.[4–7] However, recent studies have shown the unexpected possibility of converting plant polymers into liquid or fusible monocyclic products (cellulose to furans, lignin to benzenediols and methoxyphenols, chitin to pyrroles and pyridines) at relatively lower absorbed doses and higher radiation-chemical yields.[8–10] The observed differences from depolymerization indicate that liquid products are formed *via* an alternative, previously unknown, mechanism. The present work was intended to formulate the key conditions and stages of an alternative chain mechanism, which we call self-disassembly.

The self-disassembly mechanism seems to be a sequential cleavage of monocyclic units from the end of the macromolecule. In both depolymerization and self-disassembly, the splitting of a macromolecule begins with the formation of a radiation defect, a macroradical, positioned on one of the monomer units or between units. For example, in cellulose, ionizing radiation creates radical centers on C(1) or C(4) atoms[4–6] (Scheme 1). Such intermediate defects are unstable due to the discrepancy between the electron configurations of the radical (sp^2-hybridization, planar configuration) and the original monomer (sp^3 hybridization, tetrahedral configuration). Bond splitting between the defect and the intact unit is the first step towards stabilization. Such splitting occurs even at room temperature, creating one of the terminal radicals, $\mathbf{R_t(1)}$ or $\mathbf{R_t(4)}$ (Scheme 2). This splitting is a necessary and sufficient prerequisite for the well-known radiation depolymerization.

In turn, a necessary prerequisite for self-disassembly is the transfer of the radical center from the terminal position to the opposite end of the defective unit, for example, from C(1) to C(4) position. Such a transfer could destabilize the next connecting bridge. In the case of lignin whose monolignols contain conjugated

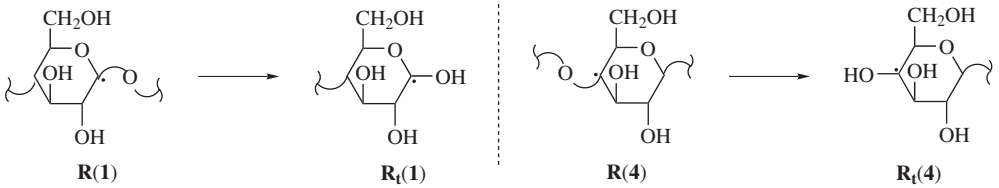


Scheme 1

aromatic bonds, a delocalized electron can directly provoke the cleavage of any connecting bridge. As a rule, the weakest lateral β-bond undergoes cleavage.[11] Original polysaccharide units do not contain double bonds. However, heating can stimulate the formation of double bonds by dehydration of the defective unit in the polysaccharide.[2,4,5] Dehydration of $\mathbf{R_t(1)}$ and $\mathbf{R_t(4)}$ is already observed at ~100 °C, whereas pyrolytic dehydration of cellulose macromolecules starts above ~200 °C.[1,7] Thus, heating makes it possible to convert terminal radicals $\mathbf{R_t(1)}$ and $\mathbf{R_t(4)}$ to allylic-type ones (Scheme 3). Accordingly, double bonds promote the transfer of a radical center within a defective unit. The new position of the radical center near the connecting bridge causes configurational tension in the polymer chain and, thus, again causes splitting of the bridge. As a result, the partially dehydrated defective unit is removed and a new radical center would emerge on the terminal unit of the truncated macromolecule. The removed units appear to be unstable and undergo heat-stimulated elimination of the most mobile small molecules, mainly, CO, CO_2, $H_2C{=}O$ or HCOOH. Such products are experimentally found in irradiated plant polymers.[2,4,5] Finally, stable furylmethanol or furfural are formed (Scheme 4).

In total, radiation generates macroradicals while proper heating causes their subsequent chain self-disassembly (the yield in cellulose is *ca.* 30 μmol J^{-1}). In particular, heating stimulates the local dehydration of the defective unit and the transfer of the unpaired electron to the next connecting bridge. Moreover, heating provokes both the expulsion of the defective unit from the macromolecule and its transformation into a stable compound, as well as the evaporation of this compound from the reaction area.

Typically, depolymerization is carried out below 100 °C, *i.e.* under conditions when the macromolecules are fixed by intermolecular and intramolecular hydrogen bonds (dissociation energy of 8–40 kJ mol^{-1}) involved in the dissipation of excess energy, as well as in the cage effect. In polysaccharides in this case, dehydration of primary radicals and their transformation into allylic ones does not occur. As a result, there is no transfer of a defect along the polymer chain. In this temperature range, partial random depolymerization proceeds, consisting in reducing the degree of polymerization without the formation of liquid products (Figure 1). For example, 480 kGy absorbed dose reduces the cellulose polymerization degree almost by a factor of 80 without producing furans.[2] When the temperature is higher than the



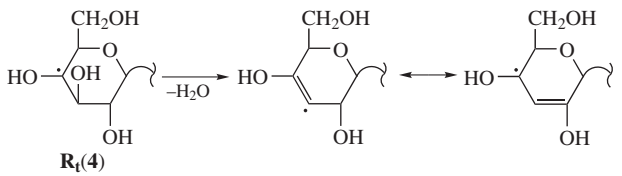
Scheme 2

pyrolysis threshold, plant polymer is converted predominantly into water, carbon dioxide and charcoal *via* complete dehydration and decarboxylation of the macromolecules (due to the simultaneous vibrational and rotational excitation of all monomeric units). At least, to ensure self-disassembly, the proper temperature should exceed the evaporation point of the target monocyclic product (for example, furans in the case of cellulose), but its value should be below the pyrolysis threshold.

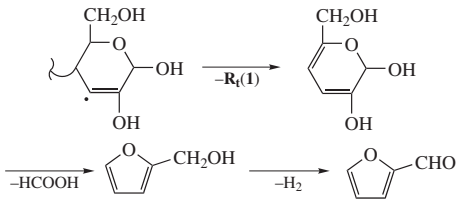
Effective chain degradation of plant polymers *via* the self-disassembly mechanism below the pyrolysis threshold is a consequence of lower thermal stability of macroradicals compared to macromolecules. In polysaccharides and polyphenols, self-disassembly is facilitated by the lower strength of the ether bridges between the units. Obviously, the final products must be immediately removed from the irradiation area in order to avoid secondary decomposition. Accordingly, favorable conditions for radiation-driven self-disassembly can be created by combining irradiation with simultaneous dry distillation. Unique 'instructions' how to disassemble the plant polymer are 'encoded' in the structural features of the radicals generated by the radiation-thermal pathway.

Self-disassembly could lead to a mono-product, since similar elementary polymer units participate in successive transformations in a uniform manner. However, various reasons can reduce efficiency and even suppress self-disassembly. High dose rate creates a high concentration of radicals and, thereby, increases the probability of radical decay *via* their recombination. Intersections and contacts of macromolecules facilitate the transfer of the unpaired electron to another chain. Branching in the macromolecule contributes to the appearance of defects of an irreproducible type. Steric factors prevent the product migration from the cage. In particular, branching in lignin macromolecule leads to a multi-type cleavage of the bonds and, thereby, extends the assortment of products.[8,10] Dense packing of surrounding molecules can prevent the migration of radical and molecular fragments. For example, allylic radicals can be converted to polyene-type radicals (Scheme 5), which are more stable and play the role of charcoal precursors.[4,5]

Cellulose seems to be the best example of a polymer suitable for self-disassembly. Unlike cellulose, the chitin monomer unit contains a large and easily cleavable acetamide side group which



Scheme 3



Scheme 4

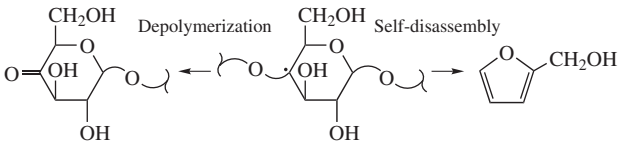
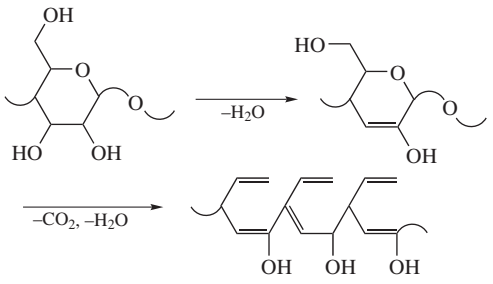


Figure 1 Key pathways of depolymerization and self-disassembly.

partially carries out the protection of the pyranose ring. In turn, lignin contains units connected by more than two bridges to other units. As a consequence, the self-disassembly process in lignin can acquire an undesirable direction. Self-disassembly requires simultaneous irradiation and heating. In the case of preliminary irradiation and subsequent heating (post-radiation dry distillation), the yield of monocyclic products is much lower (Figure 2). Obviously, the proper macroradicals generated *via* irradiation are relatively short-lived and, accordingly, decay or change configurationally in the interval between irradiation and distillation.

There are a number of spontaneous phenomena whose name contains 'self-': self-ignition, self-assembly, self-organization, self-induction, self-focusing, and some others. In fact, these phenomena occur only under certain favorable conditions and do not proceed outside these conditions. Self-disassembly is one of such phenomena since it occurs for certain types of free macroradicals only under favorable thermal conditions.

Undoubtedly, the skills of large-scale production of chemical building blocks from renewable plant materials are in great demand for further sustainable development.[12–14] In this regard, the self-disassembly of plant polymers looks like a productive and environmentally friendly access to valuable materials for green chemical synthesis. For example, the self-disassembly mechanism described above seems to be a unique way of large-scale producing furans directly from cellulose.



Scheme 5

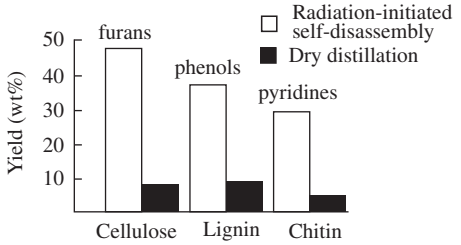


Figure 2 The yields of monocyclic products in the self-disassembly of cellulose, lignin and chitin *vs.* those in post-radiation dry distillation.

The work was carried out within the state theme AAAA-A16-116121410087-6 of the Ministry of Science and Higher Education of the Russian Federation using equipment provided by the Center for Collective Use of Physical Research Methods of the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences.

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Received: 11th April 2019; Com. 19/5879