STRUCTURAL TRANSFORMATIONS OF POLYSACCHARIDES EXPOSED TO CO₂-LASER RADIATION

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We have used IR spectroscopy to study conformational transformations of polysaccharide macromolecules (dextran, pullulan, amylose, and microcrystalline cellulose) and changes in their structural ordering when exposed to cw emission of a CO₂ laser. We have established that the structures of conformationally labile polysaccharides are the most sensitive to laser radiation. The effect of laser treatment is greatest for lower molecular weight polymers. We have observed for the first time changes in the conformational states of dextran macromolecules in the direction of an increase in the structural ordering when exposed to emission from a CO₂ laser. This quite different from purely thermal treatment, where disordering of the polysaccharides structure occurs.

Key words: polysaccharides, IR spectrum, emission from a CO₂ laser, structure, ordering, conformational transformations, lability.

Introduction. High molecular weight polymer materials are widely used in modern equipment construction, power engineering, medicine, the food industry, etc. Usually in order to achieve the required consumer properties for the polymers, their structure is modified using heat sources [1]. Recently modification of polymer materials has been accomplished by plasma treatment [2] and laser irradiation [3–12]. Using laser radiation makes it possible to control the modification of the physical structure of the material, to increase the reaction rate, the weight yield, and the purity of the products.

Some of the early research on modification of the structure of high molecular weight compounds using laser radiation was carried out at the Institute of Physics (National Academy of Sciences of Belarus) in 1974 [3]. Compared with heat treatment, it was established that there was a significant (by several orders of magnitude) shortening of the time until spectroscopic signs of crystallization appeared for cellulose triacetate films exposed to the emission of a cw CO₂ laser. In this case, substantially lower energy consumption was required compared with conventional heat sources (hot air, thermostat, IR radiation sources). Subsequent investigations [4–6] showed that the physicochemical properties, heat and light resistance of high molecular weight compounds change significantly when they are exposed to laser radiation. It has been hypothesized that the characteristic features of structural transformations of cellulose and its derivatives when exposed to laser radiation are due to transfer of energy to the macromolecules in the initial stage only along one channel: the effect on vibration of the structurally active bonds C–O and C–C, for which the stretching vibration frequencies are within the range 900–1100 cm⁻¹, where the lasing frequencies of the CO₂ laser are found at ~940 cm⁻¹ [3, 4]. Consequently, in principle it is possible to primarily supply additional energy to selectively heat specifically these bonds. The increase in the temperature of the surrounding medium that is required for onset of many processes proves to be unnecessary. The reactions occur under thermodynamically nonequilibrium conditions. The required energy is concentrated on certain bonds, predominantly structurally active bonds, as a result of the redistribution of the molecules with respect to degrees of freedom. We can assume the following mechanism for such an effect: resonance excitation of complex vibrational modes with predominant contribution to the potential energy distribution

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from vibrations involving the indicated bonds, including torsional vibrations. In this case, efficient accumulation of absorbed energy occurs in the vibrational modes, along with an increase in the conformational mobility of the structural fragments. As a result of rotation about the structurally active bonds, conformationally ordered forms of the macromolecules arise due to the effect of noncovalent intramolecular interactions. This is accompanied by breaking of weak intermolecular bonds, formation and growth of crystallization centers due to strong interaction between resonance-excited cooperative vibrations of adjacent macromolecules. After the laser irradiation stops, the structures formed are fixed into position by a new system of noncovalent intermolecular interactions [4, 5].

In this paper, we present the results of IR absorption spectroscopy studies of the structural modification of high molecular weight compounds when exposed to emission from a cw CO₂ laser.

Studied materials. The high molecular weight powdered polysaccharides dextran, pullulan, amylose, and microcrystalline cellulose:

have the same structural units, but differ in the type of chemical bonds between them ($\alpha,1 \rightarrow 6$ for dextran; $\alpha,1 \rightarrow 4$, and $\alpha,1 \rightarrow 6$ for pullulan; $\alpha,1 \rightarrow 4$ for amylose, and $\beta,1 \rightarrow 4$ for cellulose), which means the units have different mobilities relative to each other.

As we know, macromolecules of the polysaccharide dextran, which includes anhydroglucopyranose rings linked by $\alpha,1 \rightarrow 6$ bonds, are characterized by higher mobility than macromolecules with $\alpha,1 \rightarrow 6$ and $\alpha,1 \rightarrow 4$ bonds (pullulan), $\alpha,1 \rightarrow 4$ (amylose), and $\beta,1 \rightarrow 4$ (cellulose). The polysaccharides are listed in order of decrease in conformational mobility of their macromolecular chains. For this reason, the structure of such polysaccharides should respond differently to laser treatment. Furthermore, the structural rearrangement of the studied polysaccharides may depend on the length of the chains in the macromolecules (the molecular weight MW). The molecular weight dependence was studied for the example of samples of powdered dextran from Fluka (with MW 15,000 to 20,000 and 110 000) and pullulan with similar molecular weights, and also native dextran and pullulan (MW 2 000 000).

The studies were conducted on samples of polysaccharides pressed into a KBr matrix in the form of disks of diameter 3 mm and thickness 1 mm.

Experimental setup. The experimental setup we designed (Fig. 1) allows us to expose the studied high molecular weight compounds to the emission of a CO₂ laser with flux density (Δq) in the range $0.25-(1.40 \cdot 10^3)$ W/cm². In this case, the exposure time (Δt) can be varied within the range from 5 msec to tens of minutes. The emission from

Fig. 1 Optical layout of the apparatus for irradiating the samples.

CO₂ laser 1, operating in continuous wave (cw) mode with output power up to 120 W, when shutter 7 and the window of chopper 9 were open was directed by means of a KCl lens 8 onto the sample surface 10. The sample was formed by pressing a mixture of the test material and KBr in a channel located in the center of disk 11, using two steel punches. The polished disk 11, of diameter 20 mm and thickness 3 mm with a channel of diameter 3 mm, was made from quenched steel. The greater mass of the disk compared with the sample promoted additional cooling of the sample, reducing the effect of its thermal heating from exposure to the laser radiation. The latter circumstance provides a basis for connecting the changes in the IR absorption spectra observed after irradiation of the samples with the selective effect of the laser radiation, and not just with the effect of heat. In this case, the distance from the focusing lens 8 to the sample was chosen so that the diameter of the CO₂ laser radiation spot matched the diameter of the sample. We measured the laser output power using a Goldstar power meter (OPHIR, Israel). In this case, we mounted a 10A-V2-SH measurement head from the Goldstar power meter kit in place of the sample.

In order to monitor the level of laser radiation flux incident on the sample during exposure, a small fraction of the laser beam was deflected by the polished side of a rotating vane of coupler/modulator 6 toward a germanium lens 5, which focused the shunted flux onto photometric sphere 4. Taking into account the fact that the flux density in the transverse cross section of the laser beam is not uniform and may vary over time in different areas of the cross section even when the power is unchanged, the radiation is sampled from the entire transverse cross section of the beam, for which the rotating vane intersected the entire laser beam. After multiple reflection off the inner surface of the sphere, part of the laser flux, proportional to the total laser output power, entered an MG-30 pyroelectric photodetector 3. The electrical signal from the photodetector was amplified by a V6-9 selective amplifier 2 at the rotational frequency (50 Hz) of the vane of modulator 6. The photometric sphere was used to reduce the negative effect on the uncertainty of the measurements from both the band sensitivity of the detection area of the photodetector, and the time-varying nonuniformity of the radiation flux density in the transverse cross section of the laser beam (the latter is especially typical for lasers with multimode output). In order to increase the efficiency of conversion of a laser beam that was nonuniform over the transverse cross section to one that was uniform at the output of the sphere, its inner surface was lined with crumpled aluminum foil [13], having a high reflection coefficient at the laser output wavelength ($\lambda = 10.6 \mu\text{m}$). The power sampled using the described power meter was no more than 1% for a modulation duty cycle 1/133. The vane of the modulator crosses the laser beam in a time of 0.002 sec. Such parameters allowed us to consider the negative effect of the modulator as insignificant during the measurements.

The exposure time for the samples was set by chopper 9, actuated by an electric motor with a reducing gear. The chopper is a duraluminum slotted sector disk with variable opening angle. The sample exposure time Δt was determined using a Ch3-34A frequency meter 14, operating in the time interval measurement mode. The frequency meter was started at the instant the electrical signal produced by photodetector 13 appeared, and was stopped when this signal disappeared. The interval between the start and stop time Δt was lit up on the frequency meter panel, and coin-

Fig. 2. IR spectra of dextran samples (MW 110 000) before exposure to emission from a CO₂ laser (solid line) and after exposure (dashed line) for current density $q = 1100 \text{ W/cm}^2$ ($P = 77 \text{ W}$), $\Delta t = 10 \text{ msec}$ (a) and 30 msec (b).

cided with the time it took for a sector slot in disk 9 to cross the output beam from auxiliary LGN-207B He-Ne laser 12. It is specifically in this time that the emission from the auxiliary laser initiated operation of photodetector 13. Since the beam from the CO₂ laser also went through the slot in disk 9 when shutter 7 was open, the sample was also exposed during this time. The uncertainty in the sample exposure time measurement was no greater than ~1% and was mainly due to the variability in the rotation rate of chopper 9.

Changes in the structure of the compounds were detected by comparing the IR absorption spectra for the same sample before and after exposure to emission from the CO₂ laser. The absorption spectra were recorded on a JASCO (Japan) IR-810 spectrophotometer, using the BC-3 accessory, allowing us to study samples with small transverse cross section.

Measurement results. In the IR spectra of polysaccharides exposed to laser radiation, we observe changes in the structurally sensitive $1250\text{--}980 \text{ cm}^{-1}$ region, characterizing increased conformational ordering of the macromolecular chains [4, 14]. We should note that in all the examined cases, the changes in the spectra reflect an increase in ordering of the physical structure for the analyzed polymer systems, while it always decreases during heat treatment [14, 15].

In the spectra of dextran exposed to laser radiation with $q = 1100 \text{ W/cm}^2$ and $\Delta t = 10 \text{ msec}$, 20 msec , and 30 msec , which ensures an energy density of $Q = 11, 22$, and 33 J/cm^2 , respectively, we observe changes in the intensity ratios of the bands in the frequency interval $1050\text{--}1000 \text{ cm}^{-1}$ and a shift in the absorption band maximum from 1011 cm^{-1} (initial sample) to 1015 cm^{-1} (exposure with energy density $Q = 11 \text{ J/cm}^2$) and to 1019 cm^{-1} (with $Q = 33 \text{ J/cm}^2$) (Fig. 2a and b). Furthermore, increasing the input energy density to 33 J/cm^2 leads to a change in the intensity ratio of the bands at $1040\text{--}1038 \text{ cm}^{-1}$ and $1019\text{--}1011 \text{ cm}^{-1}$, which are specific for rotational isomerism [4, 14]. Note that similar changes in the spectra of dextran were observed for films obtained from aqueous solutions with

Fig. 3. IR spectra of pullulan samples before exposure to emission from a CO₂ laser (solid line) and after exposure (dashed line) for current density $q = 1100 \text{ W/cm}^2$ ($P = 77 \text{ W}$), MW 160 000, $\Delta t = 10 \text{ msec}$ (a) and 30 msec (b); and $q = 1290 \text{ W/cm}^2$ ($P = 90 \text{ W}$), MW 14500, $\Delta t = 30 \text{ msec}$ (c).

addition of the salt KCl, and were explained by the change in the relative spatial arrangement of the elementary units due to rotations about the C₁–O–C₆ bonds [14]. The results obtained provide a basis for concluding that conformational transitions of the dextran macromolecules occur when exposed to emission of a CO₂ laser under the experimental conditions indicated above.

After exposure of pullulan under the same conditions, the relative intensity increased for the bands at 1153–1149, 1078–1076, and 1040–1037 cm⁻¹ (Fig. 3a and b). Compared with dextran, the corresponding differences are less

pronounced here. When the incident flux density of the emission from the CO₂ laser is increased up to $q = 1290 \text{ W/cm}^2$, in the pullulan spectra the intensity ratio changes for the bands in the frequency range $1050\text{--}1000 \text{ cm}^{-1}$, and in addition the intensity of the bands at 1149 cm^{-1} and 1078 cm^{-1} increases (Fig. 3c).

Irradiation of amylose using a CO₂ laser ($q = 1100 \text{ W/cm}^2$, $\Delta t = 10 \text{ msec}$, 20 msec , and 30 msec) leads to an insignificant increase in the intensity of the $1152, 1078 \text{ cm}^{-1}$ bands due to the lower lability of its structural elements. In the case of cellulose, even for more significant exposures ($P = 90 \text{ W}$, $q = 1290 \text{ W/cm}^2$, $\Delta t = 50 \text{ msec}$), the changes in the spectrum are even less pronounced: the intensities of the bands at $1155, 1108, 1092 \text{ cm}^{-1}$ change insignificantly, and the 1369 cm^{-1} band is shifted.

The mobility of the molecular units of polysaccharides depends not only on the type of chemical bonds between the elementary units of their macromolecules, but also on their molecular weights, which is especially apparent in the example of the polysaccharides dextran and pullulan, characterizing a very labile structure.

Dextran and pullulan samples of similar molecular weights were irradiated successively, one after the other, so that the laser radiation flux densities in both cases were close. This makes it possible to explain the differences appearing after laser treatment in the IR absorption spectra by just the structural features of these polysaccharides.

On exposure to laser radiation with flux density $q = 730 \text{ W/cm}^2$ for $\Delta t = 20 \text{ msec}$ ($Q = 14.6 \text{ J/cm}^2$), the characteristic changes in the IR absorption spectra are observed only for dextran with MW 15,000 and 110 000. For native dextran, due to its high MW (2 000 000), and also for pullulan with MW 14,500, 160 000, and 2 000 000, due to the lower lability of the structure compared with dextran, no changes were observed in the spectra under such laser treatment conditions. When the laser radiation flux density was increased by a factor of 1.5 ($q = 1100 \text{ W/cm}^2$) with an exposure time in the range $10\text{--}30 \text{ msec}$, the changes in the IR spectra of dextran were more pronounced for samples of this polysaccharide for all molecular weights. And the changes increase as the laser exposure time increases, and consequently the input energy density Q increases from 11 to 33 J/cm^2 (Fig. 2a and b). For pullulan, for the same power density and exposure time $\Delta t = 10 \text{ msec}$ ($Q = 11 \text{ J/cm}^2$), exposure to laser radiation does not lead to substantial changes in the spectra of this polymer. When Δt is increased to 30 msec ($Q = 33 \text{ J/cm}^2$), the characteristic changes in the spectra described above appear (Fig. 3a and b). For native pullulan (MW 2 000 000), such an increase in energy is not sufficient to observe the signs of the corresponding conformational changes in the spectra.

Conclusion. Under identical laser radiation exposure conditions, structural transformations are easily accomplished in polymers with better mobility (lability) of the elementary units in their macromolecules and with minimal molecular weight. The most pronounced changes in the IR absorption spectra, evidence for a significant increase in the degree of ordering of the molecular structure when exposed to the emission from a CO₂ laser, are observed for the polysaccharide dextran with the lowest molecular weight (15000) and the highest lability of the elementary units in the macromolecule (the presence of $\alpha,1 \rightarrow 6$ bonds) compared with the other studied polysaccharides. The changes in the spectra reflect an increase in the ordering of the physical structure of the analyzed polymer samples, while the ordering of the structure always decreases under heat treatment.

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