IR-laser-stimulated spatially selective dissociation of macromolecules

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We have observed spatially selective dissociation of polymer macromolecules which selectively absorb radiation with $\lambda \simeq 2.80\,\mu$m (the stretching-vibration band of OH groups) under conditions of pulsed resonance laser action by radiation from a parametric light generator ($\tau_p \simeq 30$ ns). The nonequilibrium effect became possible because of aggregation of such macromolecules into absorbing associates (clusters) and localization of vibrational energy on them for a period of time comparable to the characteristic dissociation time. Analysis of the kinetics of selective dissociation showed that the characteristic relaxation time of the vibrational energy from excited associates is equal to $\sim 10^{-9}$ s, which is significantly longer than the characteristic intra- and intermolecular exchange times for condensed media.
We established that the degree of selectivity of dissociation increases as the degree of ordering of the packing of the macromolecules decreases. This indicates that hydrogen bonds have a significant effect on the process of deactivation of the excited macromolecules.

Intense vibrational relaxation in the condensed phase ($\tau_{vv'} \simeq 10^{-11}$–$10^{-12}$ s) is a serious obstacle to the stimulation of selective photophysical and photochemical processes by resonance laser radiation. The observation of an entire series of selective heterogeneous effects has nonetheless been reported: evaporation, desorption, and diffusion of molecules through microporous media.[1-8]

We believe that there exists another large class of substances—linear polymer macromolecules—where selective processes can in principle occur. The point is that in polymer media the linear macromolecules, interacting with one another, become organized into different types of associates (clusters). These are so-called complex chain molecules or complex molecules.[9] They contain from two to three up to several hundreds of linear molecules. It is important that complex molecules behave as autonomous structural formations.

Figure 1 shows a fragment of the molecular structure of a polymer. If such an associate selectively absorbs IR radiation, then it can be expected that vibrational energy will be localized on the associate for quite a long time. Indeed, if the vibrational excitation is weak, then the inductive energy transfer can be neglected and the vibrational relaxation will be determined primarily by the anharmonicity of the vibrations. In this case one vibrationally excited linear molecule will rapidly equilibrate with the other molecules, since all of its monomers interact directly with their environment. In the case of an aggregate of macromolecules, however, only the "boundary" molecules participate in direct transfer of vibrational energy to the environment and the aggregate will remain excited for a longer period of time. An analogous effect should be observed for separate macromolecules in regions with dense packing or even ordered crystalline packing of monomers, for block copolymers, and the globular state of macromolecules.

The mechanisms of selective action which have been studied are related to the characteristics of the supermolecular structure of polymers and are of a spatial character.

In this work is the selective dissociation of rigid-chain linear macromolecules of cellulose nitrate (CN) with IR resonance laser action on polymer associates was investigated experimentally for the first time. In choosing the substance for studying selective dissociation we took into account the fact that for cellulose nitrate the physical and chemical properties,[10,11] the characteristics of the supermolecular structure,[12-16] as well as the high-temperature thermal[17-22] and laser dissociation[23-26] have all been relatively well studied.

Sample preparation. For the experiments we specially prepared samples of cellulose nitrate in the form of a film of thickness ~ 1 mm. The samples were formed on a quartz substrate from a highly concentrated solution of cellulose nitrate in acetone (~ 4 grams of cellulose nitrate per 100 ml of solvent). The average linear size of the macromolecules was equal to $\sim (2.0–2.5) \cdot 10^3$ Å with degree of polymerization $n \simeq 400–500$. As shown in Refs. 27 and 28, for this concentration and degree of polymerization the solution is not a true solution: The macromolecules interact strongly with one another and they aggregate into associates and do not exist in solution in any other form other than as associates. This is also indicated by measurements of the viscosity of such solutions.[29] The length of an associate is equal to the average linear size of the macromolecule, and the transverse size of the associate is equal to $\sim 50–100$ Å.[30]

Associates of macromolecules of two types were present with the same concentration in the solution: cellulose mononitrate (~ 10 mass % nitrogen) and cellulose trinitrate (~ 14 mass % nitrogen). The average nitrogen concentration was equal to $\sim 12\%$, which correspond to cellulose dinitrate. The structural formulas of mono- and trinitrate are presented in Fig. 2. It is important that in cellulose trinitrate all OH groups are replaced by ONO_2 groups.

The conditions for preparing the polymer film were chosen so that when the acetone evaporated the structure of the associates present in the solution would not be destroyed and a film without pores and internal stresses would form.[27] As the solvent was removed the viscosity of the solution increased, the diffusion coefficient decreased by several orders of magnitude,[31] and the characteristic diffusion distance of the macromolecule or associate in the condensed phase was

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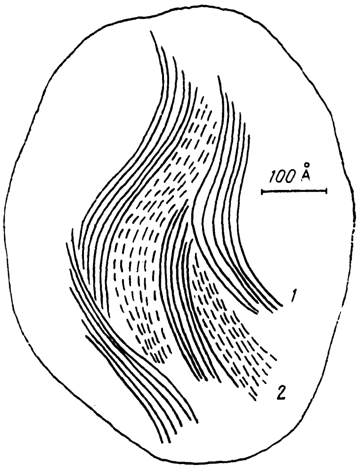

FIG. 1. Schematic diagram of the supermolecular structure of the polymer studied. The different lines show different types of associates of the macromolecules: 1—$[R(ONO_2)_3]_n$ and 2—$[R(OH)_2(ONO_2)]_n$. Here R is the part of the monomer remaining after substitution and n is the degree of polymerization.

estimated to be ~ 20 Å over 10^3 h. Thus significant displacements of macromolecules or associates relative to one another, which could destroy the structure, were excluded and the associates initially present in the solution remained in the film also.

The cellulose nitrate samples prepared in this manner contained associates of macromolecules of cellulose mono- and trinitrate, which had different spectral properties in the near-IR region of the spectrum. If radiation with $\lambda \simeq 3.43$ μm (the stretching-vibration band of the C–H group) was equally absorbed by all associates, since C–H bonds are present in all monomers, then radiation with $\lambda \simeq 2.80$ μm (the stretching-vibration band of the O–H groups) was selectively absorbed only by associates of cellulose mononitrate macromolecules.

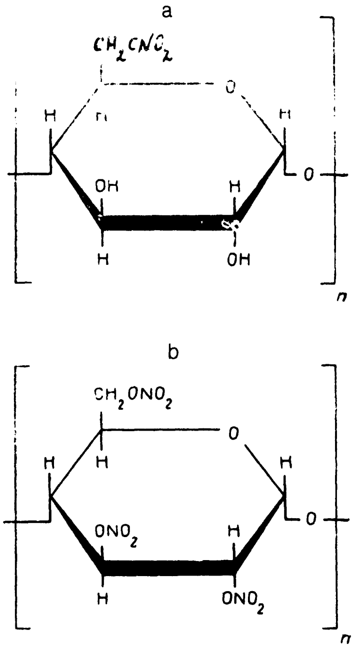

FIG. 2. Structural formulas for monomers of cellulose mononitrate (a) and trinitrate (b).

The spectrum of the samples studied in the near-IR region is presented in Fig. 3. One can see that high spectral selectivity can be achieved by irradiating cellulose mononitrate associates with radiation with wavelength $\lambda \simeq 2.80\,\mu$m.

X-Ray structural analysis of the polymer samples obtained showed that they have an amorphous crystalline structure with the degree of crystallinity ranging from 31% to 41%.

EXPERIMENTAL PROCEDURE

A parametric light generator (PLG) was specially developed as a source of IR radiation. The generator operated on the nonlinear crystal $LiNbO_3$, which made it possible to tune the wavelength of the radiation smoothly over the range 1.4–4.2 μm, which in turn made it possible to excite the stretching vibrations of OH and CH groups in the macromolecules. The energy in a pulse of radiation from the PLG was $E_p \lesssim 120$ mJ and the pulse length was $\tau_p \simeq 30$ ns.[32]

The absorption coefficients of the samples at the maxima of the vibrational bands of interest to us were equal to 350–400 cm^{-1}, i.e., the laser action was almost completely superficial and dissociation of macromolecules occurred on the surface of the sample. A time-of-flight dynamic mass spectrometer was employed effectively for the diagnostics of such processes.[33] The samples of the polymers studied were placed into the optical vacuum chamber of the mass spectrometer at a pressure $P \simeq 5 \cdot 10^{-5}$ Pa. The tunable radiation from the PLG was focused on the sample into a ~ 2 mm in diameter spot. The characteristic energy flux densities were equal to $q \simeq 10^6$–10^8 W/cm^2.

The operating conditions of the mass spectrometer made it possible to determine both the composition of the dissociation products and the velocity distribution of the molecular fragments leaving the surface of the sample. Thanks to the high power of the parametric generator, the products expanded into the vacuum in a collisionless fashion.[26] This, on the one hand, made it possible to investigate the dissociation of macromolecules directly in the condensed phase on the surface of the sample and in the absence of chemical reactions between the gaseous products formed,

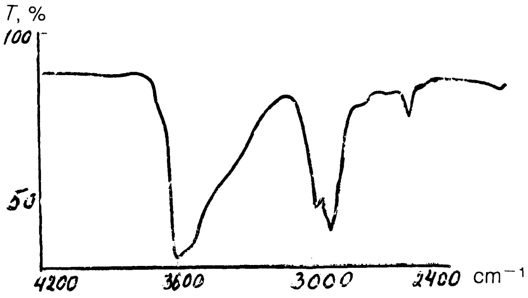

FIG. 3. IR spectrum of the prepared samples of cellulose nitrate. The thickness of the film is equal to $\simeq 30\,\mu$m.

and it enabled us, on the other hand, to determine from the velocity distribution of the fragments the effective dynamic temperature of the fragments. For collisionless expansion and $E_a/kT \gg 1$ the latter temperature is equal to the maximum surface temperature of the sample at which most of the fragments leave the surface. Here E_a is the activation energy of the dissociation reaction, k is Boltzmann's constant, and T is the surface temperature.

Thus we were able to control, apart from the composition and quantity of products formed, the surface temperature of the sample. This was fundamentally important for comparing the results of action in different vibrational bands.

EXPERIMENTAL RESULTS

The mass spectra of the dissociation products of cellulose nitrate macromolecules exposed to resonance radiation in the stretching-vibration band of CH and OH groups were compared. We underscore the fact that in the case of excitation of OH vibrations we acted only on the associates of cellulose mononitrate, which have OH molecular groups. In addition, the associates comprising the polymer under study have a similar chemical structure (see Fig. 2), and therefore the dissociation products of their macromolecules are also the same. The differences can be only quantitative.

The excitation of CH vibrations must, of course, result in thermodynamically equilibrium dissociation of macromolecules, since the C–H bonds are present in equal amounts in the monomers of associates of both types, while the vibrational relaxation time ($\tau_{VV'} \simeq 10^{-11}$–$10^{-12}$ s; Ref. 34) is significantly shorter than the characteristic chemical reaction time for our conditions $\tau_d \sim 10^{-9}$ s (Ref. 26).

The thermal dissociation of cellulose nitrate macromolecules under the action of pulsed resonance radiation from the PLG in the stretching-vibration band of CH groups ($\lambda = 3.2$–$3.6\,\mu$m) was investigated in detail in Refs. 25 and 26. It was shown that dissociation occurs in two independent channels: detachment of a NO_2 group with activation energy $E_1 \simeq 1.7$ eV and scission of the glucopyronose ring ($E_2 \simeq 1.9$ eV) with formation of the principal products H_2O, CH_2O, CO, and CO_2. It was established that the quantitative ratios of the products formed depend significantly on both the flux density q (actually the surface temperature of the sample) and the absorption coefficient η for the laser radiation. This is connected with the fact that secondary chemical reactions occur in the condensed phase between the products of dissociation of the macromolecules. However in some range of values of the parameters of the laser radiation (q, η) only the primary monomolecular dissociation reactions of the polymer chains occur. An analogous picture is also observed in the case of action in the stretching-vibration band of OH groups. It is obvious that the secondary reactions significantly distort the initial picture of the dissociation. It follows that the results of the laser action in different vibrational bands can be compared only if identical thermal conditions are also maintained in the absence of secondary reactions.

These conditions can be met with the help of a parametric generator of light, whose wavelength can be tuned smoothly within one of the selected absorption bands, and by using the time-of-flight spectra to monitor the surface temperature.[32]

Figure 4 shows the averaged mass spectra of the dissociation products of cellulose nitrate macromolecules. These spectra were obtained with excitation of the stretching vibrations of OH and CH groups under the conditions described above (the surface temperature was $T_s \simeq 1500$ K and the absorption coefficient was $\eta \simeq 350$ cm^{-1}). The main mass peaks are A_{28}, A_{29}, A_{30}, A_{44}, and A_{46} (A_i is the amplitude of the peak of the corresponding mass). These peaks correspond to the molecules CO, CHO, CH_2O, NO, CO_2, and NO_2. Significant differences are observed in the mass spectra. This is expressed in the fact that the amplitude of the mass peaks A_{28} (CO), A_{29} (CHO), and A_{44} (CO_2) is higher for $\lambda \simeq 2.80\,\mu$m than for $\lambda \simeq 3.43\,\mu$m. At the same time, the mass peak A_{46} (NO_2) with $\lambda \simeq 2.80\,\mu$m is smaller than A_{46} with $\lambda \simeq 3.43\,\mu$m.

The mass spectrum obtained with $\lambda \simeq 3.43\,\mu$m has the form characteristic for thermal dissociation of cellulose dinitrate.[19] Analysis of the composition shows that $\sim 14\%$ (by mass) of the dissociation products consists of nitrogen. This is even somewhat higher than the average nitrogen content of the sample. This is understandable, since the detachment reaction of NO_2 group has the lowest activation energy ($E_1 \simeq 1.7$ eV).

The nitrogen content in the products obtained with radiation wavelength $\lambda \simeq 2.80\,\mu$m is only $\sim 10\%$, and it decreases as the flux density increases. In addition, in the mass spectrum the amplitudes of the mass peaks belonging to the dissociation products of the glucopyronose ring—A_{28} (CO), and A_{29} (CHO)—are relatively high. Thus it can be concluded that the mass spectrum observed when the sample

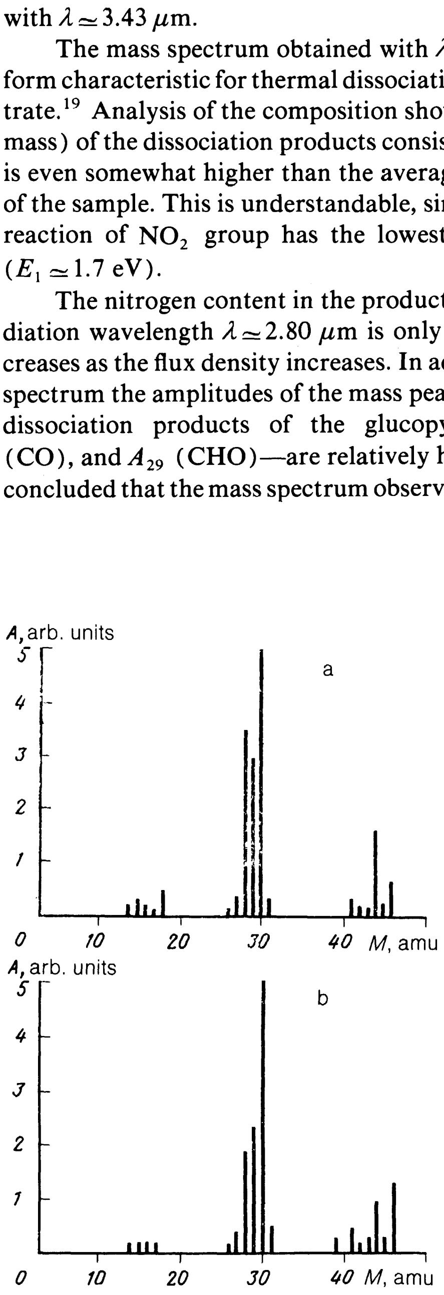

FIG. 4. Mass spectra of the products of dissociation of macromolecules irradiated in the stretching-vibration band of OH groups ($\lambda = 2.80\,\mu$m) (a) and the CH groups ($\lambda = 3.43\,\mu$m) (b).

is irradiated with radiation of wavelength $\lambda \simeq 2.80\,\mu\text{m}$ (the stretching-vibration band of OH groups) is characteristic for the dissociation of a sample with low nitrogen content, i.e., actually for dissociation of cellulose mononitrate macromolecules, which directly absorb the radiation.

In analyzing the differences in the mass spectra we examined the possibility that the molecular fragments formed undergo multiphoton dissociation in the field of the resonance laser radiation incident on the sample.[35] Indeed, it can happen that in the case of irradiation in the stretching-vibration bands of OH and CH groups thermodynamically equilibrium dissociation of the macromolecules of the polymer in the condensed phase occurs and that the difference in the mass spectra is governed by the IR resonance multiphoton dissociation of the gaseous products. The gaseous products are formaldehyde CH_2O and also a number of other molecular fragments (formic acid CH_2O_2, ethyl alcohol and dimethyl ether C_2H_6O, water H_2O, etc.[20-22]), which have O–H and C–H bonds and are formed in small quantities when cellulose nitrate macromolecules dissociate. It is these fragments that are, in particular, responsible for the presence of the so-called low-mass peaks in the mass spectrum: A_{16}, A_{17}, A_{26}, A_{27}, A_{31}, A_{41}, A_{42}, A_{43}, and A_{45}. Estimates show that the fraction of these products in the mass spectrum (with the exception of formaldehyde) is less than 3–6%. This means that their possible multiphoton dissociation results in a change of the mass spectra by the same order of magnitude. The observed difference is, however, significantly larger.

Thus only multiphoton dissociation of formaldehyde, whose molecule CH_2O contains C–H bonds (there are no O–H bonds) and in principle can dissociate with absorption of radiation with $\lambda = 3.43\,\mu\text{m}$, can appreciably affect the mass spectra. This process has been studied quite well[36] and results in the formation of CO (28 amu) and H_2 (2 amu). If it is assumed that it does in fact occur, then under identical thermal conditions and irradiation with radiation in the absorption bands of OH and CH the ratio $(A_{28}/A_{30})_{3.43\,\mu\text{m}}$ should be larger than the ratio $(A_{28}/A_{30})_{2.80\,\mu\text{m}}$, and this contradicts the obtained mass spectra.

We also note that when effective multiphoton dissociation of formaldehyde occurs an intense hydrogen peak, which is absent, should occur in the mass spectra. In addition, if it is assumed that there is no spatial selectivity and thermodynamically equilibrium dissociation of cellulose nitrate macromolecules occurs, then the quantitative elemental composition of the products, i.e., the quantity of H, C, O, and N should be the same in the case of irradiation in both the OH and CH absorption bands. For nitrogen, at least, as shown above, this does not happen.

Thus the possible multiphoton dissociation of formaldehyde and a number of other products in the gas phase either does not occur or it does not significantly affect the mass spectra. The discrepancies are, however, caused by the predominant (spatially selective) dissociation of cellulose mononitrate macromolecules with absorption of radiation with $\lambda = 2.80\,\mu\text{m}$.

The effect was observed in quite a wide range of flux densities q. Figure 5 shows the ratio (A_{29}/A_{46}) as a function of q for $\lambda \simeq 2.80\,\mu\text{m}$ and $\lambda \simeq 3.43\,\mu\text{m}$. The choice of this criterion for estimating selectivity seems to us to be justified, since A_{29} (CHO) is a characteristic product of dissociation of cellulose mononitrate macromolecules, i.e., macromolecules which directly absorb radiation with $\lambda \simeq 2.80\,\mu\text{m}$, and A_{46} (NO_2) is a characteristic product of dissociation of cellulose trinitrate macromolecules.

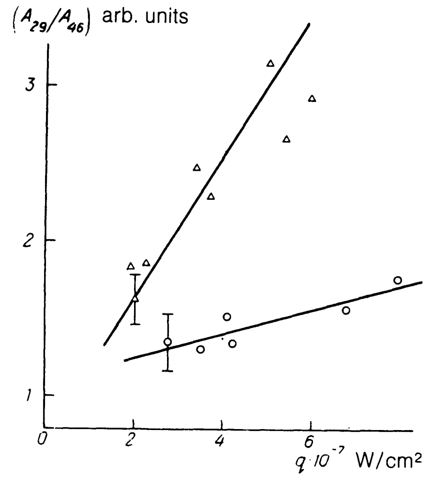

FIG. 5. The relative yield A_{29}/A_{46} of the products of dissociation of the macromolecules as a function of the laser radiation flux density q: $\lambda = 2.80\,\mu\text{m}$ (△) and $3.43\,\mu\text{m}$ (○).

One can see that

$$(A_{29}/A_{46})|_{\lambda=2.80\,\mu\text{m}} > (A_{29}/A_{46})|_{\lambda=3.43\,\mu\text{m}}$$

for q ranging from 10^7 up to $6\cdot 10^7$ W/cm^2, and, this difference tends to increase as q increases.

DISCUSSION OF EXPERIMENTAL RESULTS

Relaxation of vibrational energy within one monomer and therefore within an associate occurs very rapidly ($\tau_{VV'} \simeq 10^{-11}$–$10^{-12}$ s).[34] The final thermalization of the sample is associated with deactivation of the excited associates and occurs, as already mentioned above, significantly more slowly. The observed selective dissociation occurs even after an equilibrium distribution over vibrational modes is established within an associate and is of a statistical character.

We now analyze the dissociation kinetics. In the thermodynamically equilibrium case ($\lambda \simeq 3.43\,\mu\text{m}$) the yield of the dissociation product in the ith channel is determined by the activation energy E_i and the surface temperature. The ratio A_{29}/A_{46} is given by the following expression:

$$A_{29}/A_{46} = C_1 (b_{29}/b_{46}) \exp(-\Delta E/kT). \qquad (1)$$

Here C_1 is a constant; b_{29} and b_{46} are stoichiometric factors (for example, b_{46} is the number of substituted NO_2 groups in the monomer); ΔE is the difference of the activation energies of the formation of the two products and is equal to ~ 0.2 eV;[26] and, T is the temperature.

In the case of resonant excitation in the stretching-vibration band of OH groups ($\lambda \simeq 2.80\,\mu\text{m}$) in the ideal case, when vibrational energy is not exchanged between associates, only macromolecules which absorb radiation and whose associates can be assigned a temperature T_k will dissociate. Then we have

$$\beta=\left(\frac{A_{29}}{A_{46}}\bigg|_{\lambda=2,80\ \mu m}\right)\bigg/\left(\frac{A_{29}}{A_{46}}\bigg|_{\lambda=3,43\ \mu m}\right)$$

$$=K\exp\left[-\Delta E\left(\frac{1}{kT_k}-\frac{1}{kT}\right)\right]. \qquad (2)$$

Here $K = 2$ is the ratio of the number of substituted groups, averaged over the sample, in the monomer to the quantity b_{46} for weakly substituted associates. Since the concentrations of associates of each type are the same, in the case that the absorption coefficients for the CH and OH bands are close and the flux densities q are the same $T_k \simeq 2T$.

The surface temperature in the case of equilibrium dissociation was determined from the time-of-flight spectra of the products and reached ~ 1500 K. Substituting into Eq. (2) the numerical values we obtain

$$\beta \approx 4. \qquad (3)$$

It is obvious that in the other extreme case, when the characteristic dissociation time τ_d of the excited macromolecules is significantly longer than their vibrational relaxation time, $\beta = 1$.

The intermediate case is observed in the experiment: $\beta \sim 1.8$ for $q \simeq 6\cdot 10^7$ W/cm^2. Thus the excited molecules, in addition to dissociating, are also appreciably deactivated. Nonetheless the characteristic time of this process τ_r under our conditions does not exceed the dissociation time τ_d. We estimate τ_d with the help of an expression obtained in Ref. 37 for the dissociation probability:

$$w \approx \frac{LkT}{2\pi\hbar}\left[1-\exp\left(-\frac{\hbar\omega_{\text{eff}}}{kT}\right)\right]\exp\left(-\frac{E_a}{kT}\right).$$

Here L is a statistical factor of the order of unity, E_a is the activation energy for scission of the glucopyronose ring, equal to 1.9 eV, and ω_{eff} is an effective frequency, which usually is of the order of 10^{14} s^{-1}. We find that $\tau_d \simeq 10^{-9}$ s. Therefore the characteristic deactivation time of the excited macromolecules (actually the vibrational relaxation time) $\tau_r \simeq 10^{-9}$ s, which is significantly longer than the intermode exchange time for condensed media.

The obtained experimental results and the estimates made above show that vibrational energy is localized on the absorbing polymer associates at least during a period of time that is long enough for dissociation reactions of the macromolecules to occur; this is what makes it possible to talk about spatially selective dissociation.

We observe that the degree of selectivity of dissociation depends on the degree of crystallinity of the polymers studied (see Table I). It is well known that the crystal structure of cellulose and its derivatives (in particular, cellulose nitrate) is formed by means of hydrogen bonds.[38] The higher the degree of crystallinity of the polymer, the more hydrogen bonds between cellulose nitrate macromolecules are formed, both within one associate and between associates. The existence of such bonds leads to the appearance of an additional channel of relaxation of vibrational energy and exchange of energy between associates, and this decreases the degree of spatial selectivity. For this reason, the effect was all the stronger the lower the degree of crystallinity of the samples. The result obtained by irradiating amorphous (according to x-ray structural analysis) cellulose nitrate is interesting from this point of view. Commerical nitrate, employed as raw material for producing celluloid, was used. Its nitrogen content was equal to $\sim 7\%$, which corresponded to a degree of substitution of OH groups by ONO_2 groups in the monomer of ~ 0.9 (in contrast to the specially prepared samples, where this indicator was equal to two). An analogous effect of selective dissociation of macromolecules was also observed in this case; this was also manifested in different mass spectra obtained with irradiation in the OH and CH absorption bands.

Since intra- and intermode relaxation of vibrational excitation is fast, it is difficult to conjecture that selectivity occurs at the level of one monomer. It is well known, however, that for a low (< 1) degree of nitration of cellulose the nitration along the polymer chain departs significantly from equilibrium.[10] As a result we obtain a block copolymer, where both substituted (nitrated) sections of a chain and unsubstituted, essentially cellulose, sections are present in the macromolecules. Strong disordering of the macromolecules leads to weak coupling of the molecules with one another and, therefore, to weak exchange of energy between them. In addition, as the experiments showed, when the molecules are irradiated with 2.80 μm radiation the unsubstituted (cellulose) sections of the macromolecules, which selectively absorbed this radiation, predominantly dissociate.

TABLE I.

α, %	β
41±1	1,23±0,15
36±1	1,40±0,15
31±1	1,80±0,15

Note: α is the degree of crystallinity of the sample according to x-ray structural analysis and β is defined in the text.

BASIC CONCLUSIONS

1. We observed spatially selective dissociation of macromolecules irradiated with resonance IR laser radiation on the surface of polymers with excitation of the molecular stretching vibrations. This effect results from a significant increase of the characteristic vibrational relaxation time (up to 10^{-9} s) for the excited macromolecules aggregated into associates; this time is comparable to the dissociation time of the macromolecules.

2. The selectivity of dissociation was observed to increase as the degree of crystallinity of the polymer samples decreased. This indicates that the hydrogen bonds forming the supermolecular structure significantly affect the process of deactivation of the excited molecules.

3. The experiments demonstrated that it is in principle possible to stimulate with laser radiation selective chemical reactions in polymers at the level of supermolecular structures.

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