

Nonequilibrium dissociation of cellulose nitrate macromolecules by resonant IR laser light

A. V. Barinov, Yu. A. Bakhirkin, Yu. A. Bykovskii, S. I. Martynov,
A. A. Chistyakov, and A. I. Shcherbakov*

Moscow Engineering-Physics Institute, 115409 Moscow, Russia

**D. I. Mendeleev Moscow Chemical-Technological Institute, 125820 Moscow, Russia*

(Submitted 2 June 1993)

Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 1, 23–27 (10 July 1993)

A nonequilibrium dissociation of polymer macromolecules in the condensed phase by resonant IR laser light has been observed. The effect stems from particular features of the absorption of laser light by irregularities of the supermolecular structure of polymer chains and of the relaxation of vibrational energy along the long macromolecules of an amorphous-crystalline polymer. The extent to which the dissociation deviates from equilibrium increases with increasing disorder of the macromolecules.

A spatially selective dissociation of polymer micromolecules which selectively absorb IR laser light was reported in Ref. 1. A nonequilibrium effect is possible in this case because the macromolecules gather into light-absorbing clusters, and vibrational energy localizes at these clusters for a time comparable to the dissociation time.

We are reporting here the first observation of a selective (nonequilibrium) dissociation of cellulose nitrate macromolecules in the condensed phase for samples in which there is no clustering of molecules, so the effect described in Ref. 1 could not occur. Research in this direction is pertinent to laser initiation of selective nonequilibrium photophysical and photochemical processes in the interior and at the surface of a condensed phase.

The test samples were cellulose nitrate films 0.1–0.2 mm thick. The linear dimension of the macromolecules was $(2.5\text{--}5.0) \times 10^3 \text{ \AA}$, and the degree of polymerization was 500–1000. In the cellulose nitrate molecules, the $-\text{OH}$ cellulose groups are replaced by $-\text{ONO}_2$ groups. Samples with various degrees of substitution \bar{X} (on the average over the sample) were used: from $\bar{X} \simeq 3$, in which case all three $-\text{OH}$ groups in each monomer are replaced by $-\text{ONO}_2$ groups (complete substitution), to $\bar{X} \simeq 0.9$. In this case only one of each three $-\text{OH}$ groups of a monomer is replaced by an $-\text{ONO}_2$ group, on the average over the sample. With increasing degree of substitution, the degree of order in the packing of macromolecules increases (actually, the degree to which the sample is crystalline increases).^{2,3} The samples with $\bar{X} < 1.75$ were amorphous (according to x-ray structural analysis). The degree of crystallinity of these samples increases with increasing degree of substitution, reaching $\sim 40\%$ at complete substitution.

To excite the valence vibrations of the macromolecules we used a parametric light source based on a LiNbO_3 crystal, with an output wavelength adjustable continuously over the range 1.40–4.20 μm . The energy in a pulse was $E \simeq 40 \text{ mJ}$, and the pulse

length was ≈ 10 ns.⁴ Test samples were placed in an optical vacuum chamber of a mass spectrometer and held at a pressure $P \approx 5 \times 10^{-5}$ Pa. The tunable light from the parametric source was focused onto the sample in a spot ~ 1 mm in diameter. The typical light intensity was 10^7 – 10^8 W/cm². The dissociation products were studied by the mass-spectrometric procedure described in detail in Ref. 5.

EXPERIMENTAL RESULTS

We compared the mass spectra of the products of the dissociation of the cellulose nitrate macromolecules during illumination in the bands of the O–H and C–H valence vibrations ($\lambda = 2.80$ μm and $\lambda = 3.43$ μm , respectively), for samples differing in the degree of substitution of –OH groups by –ONO₂ groups. This comparison was carried out under identical thermal conditions, i.e., at identical surface temperatures T of the samples illuminated at the different wavelengths and with identical temperature gradients ($-\partial T/\partial z$) (z is the coordinate along the axis perpendicular to the surface of the sample, directed perpendicular to the surface). To arrange these conditions we selected identical light intensities for exciting the O–H and C–H bands, and we used wavelengths at which the absorption coefficients k_{OH} and k_{CH} were identical. In a special experiment we checked to ensure that there was no deformation of these absorption bands during the application of light at the specified intensities to the polymer. Such a deformation has been observed for other condensed media, e.g., water and ethyl alcohol, during an intense resonant IR effect on the O–H absorption band.^{6,7} The surface temperature was monitored on the basis of the time-of-flight spectra of dissociation products.⁵

The excitation of C–H valence vibrations ($\lambda = 3.43$ μm) definitely leads to a purely thermal dissociation for all samples. This result is understandable, since the C–H bond is present in each monomer, and the intermode relaxation in polyatomic molecules is a very rapid process ($\sim 10^{-11}$ – 10^{-12} s; Ref. 8). Comparison of the mass spectra of the dissociation products during illumination in the O–H and C–H absorption bands for samples with a degree of substitution $\bar{X} > 1.8$ —these samples were amorphous-crystalline samples according to x-ray analysis—showed that they agreed within the experimental error ($\sim 5\%$ of the height of each mass peak). This agreement is evidence that the dissociation is of a thermal nature even in the case of the excitation of the O–H valence vibrations ($\lambda = 2.80$ μm). For samples with an average degree of substitution $\bar{X} < 1.75$ —these are amorphous samples—we see a significant difference between the mass spectra (Fig. 1), and this difference increases with decreasing \bar{X} . As in Ref. 1, this situation is reflected in a higher amplitude of the $A_{28}(\text{CO})$, $A_{29}(\text{CHO})$, $A_{30}(\text{CH}_2\text{O})$, $A_{44}(\text{CO}_2)$ mass peaks at $\lambda = 2.80$ μm than at $\lambda = 3.43$ μm . On the other hand, $A_{46}(\text{NO}_2)$ at $\lambda = 2.80$ μm is smaller than A_{46} at $\lambda = 3.43$ μm . The dissociation products CO, CH₂O (this is the parent peak for the CHO fragment), and CO₂ have an identical activation energy $E \approx 1.9$ eV; they usually form as the result of a breaking of a glucopyrazid ring.⁹ The molecular fragment NO₂(A_{46}) is a characteristic dissociation product of substituted (nitrated) parts of macromolecules; the activation energy for its formation is ≈ 1.7 eV.¹⁰ The observed differences in the mass spectra can be characterized as resulting from a stimulation by the laser light of nonequilibrium reactions involving the dissociation of cellulose nitrate

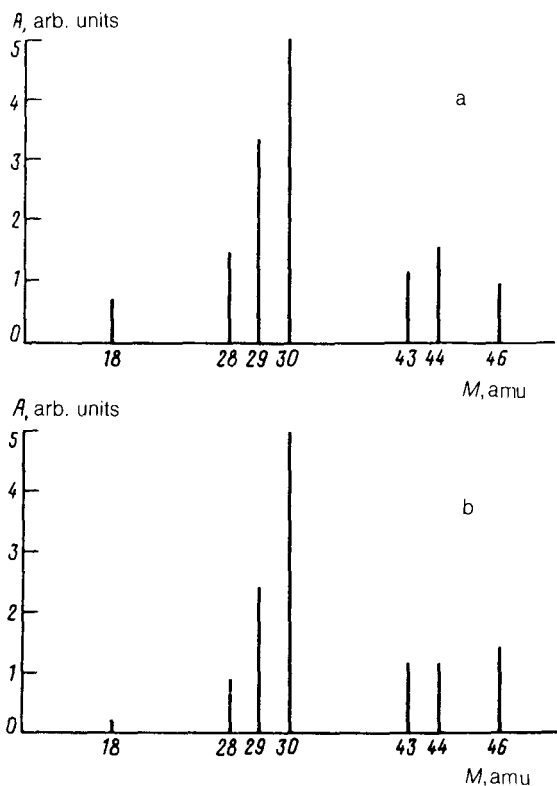


FIG. 1. Fragments of mass spectra of the cellulose nitrate dissociation products with $\bar{X} \approx 1.5$ during illumination in two valence-vibration bands: a—OH ($\lambda = 2.80 \mu\text{m}$); b—CH ($\lambda = 3.43 \mu\text{m}$). The measurement error amounts to $\sim 5\%$ of the height of each mass peak.

macromolecules in the condensed phase as the external agent acts in a resonant fashion on the OH valence vibration band ($\lambda = 2.80 \mu\text{m}$). This effect is manifested in the circumstance that the fraction of the products of the dissociation of the glucopyrazid ring with the higher activation energy is higher than at thermodynamic equilibrium. The NO_2 fraction can be characterized quantitatively by the ratio A_{29}/A_{46} . In place of A_{29} we could use the yield of other dissociation products which are formed as a result of the breaking of the glucopyrazid ring of the monomer, e.g., $A_{28}(\text{CO})$ and $A_{44}(\text{CO}_2)$, since all have the same activation energy. The extent to which the dissociation deviates from equilibrium can thus be characterized by the parameter

$$\beta = (A_{29}/A_{46})_{2.80\mu\text{m}} / (A_{29}/A_{46})_{3.43\mu\text{m}}$$

Figure 2 shows a plot of β versus \bar{X} . For $\lambda = 3.43 \mu\text{m}$, as we have already mentioned, we are dealing with a purely thermal (equilibrium) dissociation, for which the value

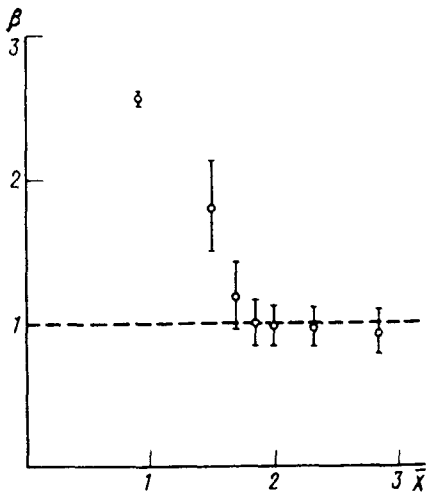


FIG. 2. Extent of the deviation for equilibrium (the degree of selectivity) of the dissociation, β , versus the degree of nitration, \bar{X} , of the test samples of cellulose nitrate polymers (see the text proper regarding β).

of the parameter β is one. The increase in this parameter which is observed at $\lambda = 2.80 \mu\text{m}$ for the samples with $\bar{X} < 1.75$ signifies the initiation of a nonequilibrium dissociation of the cellulose nitrate macromolecules in this case.

The observed effect cannot be explained in terms of a nonequilibrium distribution of vibrational energy within each monomer, since the time scales for $V-V'$ relaxation in this case are $\sim 10^{-11}$ – 10^{-12} s, much shorter than the typical times for the dissociation reactions under our conditions ($\sim 10^{-9}$ s). We believe that the explanation should be sought in particular features of the supermolecular structure of the amorphous polymers. It is now regarded as an established fact that amorphous polymers contain microscopic blocks (i.e., regions of a close packing of macromolecules) (Fig. 3), which serve as physical bonds or connections between macromolecules.¹¹ The existence of such supermolecular formations causes the substitution to be nonuniform along the molecular chain: It causes variations in deuteration or, as in the case at hand, in the replacement of $-\text{OH}$ groups by $-\text{ONO}_2$ groups (a variation in nitration). In

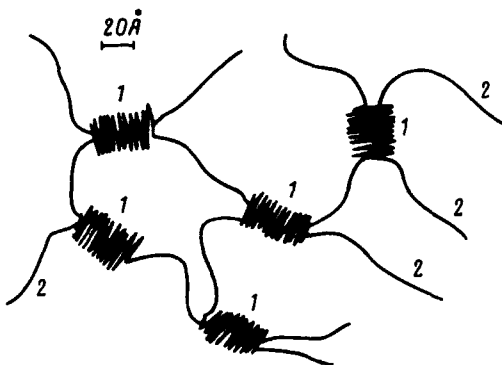


FIG. 3. Schematic diagram of the supermolecular structure of the polymers studied. The numbers specify various parts of polymer chains: 1—Microscopic blocks with a close packing and a low degree of substitution (effectively cellulose regions), which absorb light with $\lambda = 2.80 \mu\text{m}$ selectively; 2—amorphous regions with a high degree of substitution.

the microscopic blocks, by virtue of the close packing, the degree of substitution is lower than elsewhere in the macromolecules. These microscopic blocks are essentially cellulose regions of the polymer chains, and they absorb primarily at $\lambda = 2.80 \mu\text{m}$. The pronounced disorder of the macromolecules of amorphous polymers (the samples with $\bar{X} < 1.75$ are all amorphous) results in a weak coupling of these molecules with each other and thus a poor exchange of energy. The primary relaxation channel is therefore the migration of vibrational energy directly along the polymer chains. The relaxation time can be estimated from¹² $\tau_V = N/2\pi cK$, where N is the number of monomers between blocks, c is the velocity of light, and K is the anharmonicity constant. For $N \sim (10^2 - 10^3)$ and $K \sim 1 \text{ cm}^{-1}$ we have $\tau_V \sim (5 \times 10^{-10} - 5 \times 10^{-9}) \text{ s}$. The vibrational relaxation time is thus comparable to the characteristic time of the dissociation reaction, with the implication that the mechanism proposed here is real.

The reason why there is no nonequilibrium dissociation (i.e., a dissociation which is spatially selective in terms of microscopic blocks) for the amorphous-crystalline polymers (Fig. 2; $\bar{X} > 1.8$) is the large number of hydrogen bonds, which form the amorphous-crystalline structure and which play an important role in the intermolecular vibrational relaxation of the excited macromolecules. An additional channel for the migration of absorbed energy between polymer chains comes into play (this is not a migration along these chains, as in the case of the amorphous samples). The nonequilibrium dissociation of macromolecules was thus observed only at amorphous cellulose nitrate polymers. The increase in the deviation from equilibrium (an increase in the selectivity) of the dissociation with decreasing degree of substitution may be due to two factors: A low average degree of substitution leads to (first) a greater degree of nonuniformity of this dissociation¹³ and (second) a greater degree of disorder of the macromolecules.^{2,3} The latter effect ultimately leads to a low efficiency of the intermolecular relaxation and to a localization of the laser excitation at irregularities of the supermolecular structure, at least for a time comparable to the dissociation time.

¹ Yu. A. Bakhirkin, Yu. A. Bykovskii, V. I. Luksha *et al.*, Zh. Eksp. Teor. Fiz. **100**, 1739 (1991) [Sov. Phys. JETP **73**, 959 (1991)].

² S. Watanabe, J. Hayashi, and K. Imai, J. Polym. Sci. **23**, 809 (1968).

³ R. M. Myasnikova, A. F. Sviridov, E. F. Titova *et al.*, Kristallografiya **29**, 247 (1984) [Sov. Phys. Crystallogr. **29**, 146 (1984)].

⁴ Yu. A. Bakhirkin, Yu. A. Bykovskii, V. A. Ukrainitsev *et al.*, Kristallografiya **36**, 1226 (1991) [Sov. Phys. Crystallogr. **36**, 694 (1991)].

⁵ Yu. A. Bykovskii, M. M. Potapov, V. A. Ukrainitsev *et al.*, Khim. Vyssh. Energ. **21**, 361 (1987).

⁶ K. L. Vodopyanov, Zh. Eksp. Teor. Fiz. **97**, 205 (1990) [Sov. Phys. JETP **70**, 114 (1990)].

⁷ H. Graener, T. Q. Ye, and A. Laubereau, J. Chem. Phys. **91**, 1043 (1989).

⁸ V. M. Akulin and N. V. Karlov, *Intense Resonant Interactions in Quantum Electronics* (Nauka, Moscow, 1987), p. 227.

⁹ Yu. A. Bakhirkin, Yu. A. Bykovskii, A. F. Sviridov *et al.*, Khim. Fiz. **9**, 1030 (1990).

¹⁰ S. L. Madorsky, *Thermal Degradation of Polymers* (Wiley, New York, 1964).

¹¹ G. M. Bartenev and S. Ya. Frenkel', *Polymer Physics* (Khimiya, Leningrad, 1990), p. 94.

¹² V. S. Letokhov, *Nonlinear Selective Photoprocesses in Atoms and Molecules* (Nauka, Moscow, 1983), p. 356.

¹³ N. M. Bikales and L. Segal, *Cellulose and Cellulose Derivatives* (Wiley, New York, 1971).

Translated by D. Parsons