Translated from *Uspekhi Khimii* **63** 644–663 (1989) U.D.C. 541.64-539.199

Mechanodegradation of polymers. The method of molecular dynamics

L S Zarkhin, S V Sheberstov, N V Panfilovich, L I Manevich
Institure of Chemical Physics, USSR Academy of Sciences, Moscow

ABSTRACT. The experimental results in the field of the mechanodegradation of polymers, indicating significant differences between this process and thermal degradation, are discussed; the mechanism of both processes have been subjected to a comparative analysis. The principal results obtained by the method of molecular dynamics in the study of related processes such as mechanodegradation and the effect of shock waves are examined. Attention is concentrated on the mechanisms of ruptures, the formation of excited low-molecular-weight products, and the process energetics. The prospects for further research are discussed.

The bibliography includes 30 references.

Contents

I. Introduction 381
II. The application of the method of molecular dynamics 382
III. Characteristic features of the mechanodegradation of polymer chains 385
IV. Principal results and prospects 392

I. Introduction

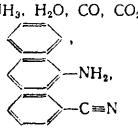
Mechanodegradation is one of the main chemical processes occurring in polymers both during their processing and during their use under load. The most effective physical method for the investigation of molecular mechanodegradation products is mass spectrometry.[1-5]

In the field of the mechanodegradation of polymers, it is now possible to distinguish two groups of experimental facts on the explanation of which the understanding of the mechanism of this process depends to a large extent. The first group includes results indicating a significant difference between the compositions of the molecular thermal degradation and mechanodegradation products (Table 1). For a number of polymers investigated by different workers[1-3] by mass spectrometry, it has been established that heavy fragments characteristic of thermal degradation are completely absent from the mechanodegradation products. The formation of only light products in mechanodegradation apparently shows that the vibrational energy is distributed significantly non-uniformly in mechanodegradation and is localised in regions whose size does not exceed 10 Å. This result is difficult to understand within the framework of the generally accepted thermofluctuation concept.[6]

The second group of experimental facts, which does not fit within the framework of the thermofluctuation concept, is the discovery of high-energy molecular products of the mechanodegradation of a series of polymeric materials (Table 2).[5] A linear polymer—poly(methyl methacrylate) (PMMA), a network epoxide polymer based on the diglycidyl ether of resorcinol and *m*-phenylenediamine (DGER–MPDA), and a composite material (ebonite) have been investigated. Table 2 shows that the molecular mechanodegradation products—both the main products (MMA, acetaldehyde) and the occluded water—have extremely high kinetic energies of translational motion ranging from 0.25 to 0.70 eV, which corresponds to translational temperatures ranging from 2000 to 5400 K.

The impossibility of explaining the results described above within the framework of the thermofluctuation concept necessitates a theoretical study of the mechanodegradation of polymers by a method which would be free from *a priori* postulates similar to those

Table 1. The molecular products of the thermal degradation and mechanodegradation of polymers.

Polymer	Volatile thermal degradation products	Volatile mechanodegradation products	Agreement between product compositions	Refs.
Poly(methylmethacrylate) (PMMA)	monomer	monomer	ec	[1]
Polystyrene (PS)	monomer, oligomers	monomer, dimer	no	[1]
Poly-α-methyl-styrene-(isotactic) (P-α-MS)	monomer	monomer	yes	[1]
Polyformaldehyde (PFA)	monomer	monomer, unidentified products	no	[1]
Polyethylene (PE)	low-molecular-weight saturated and unsaturated hydrocarbons	low-molecular-weight saturated and unsaturated hydrocarbons	?	[1]
Polypropylene (PP)	low-molecular-weight saturated and unsaturated hdyrocarbons	low-molecular-weight saturated and unsaturated hydrocarbons	?	[1]
Polyacrylonitrile (PAN)	HC ≡ N, monomer	unidentified products	no	[1]
Nitrocellulose (NC)	CO, CO_2, H_2O, NO, NO_2, CH_2O	CO, CO_2, H_2O, CH_2O	no	[1]
Polycapramide (PCA)[1]	H_2O, CO_2, NH_3, hydrocarbons	CO_2, NH_3, hydrocarbons	no	[1]
Polyepoxide	H_2, CO, CH_4, C_2H_4, C_2H_6, C_6H_6, C_8H_8	H_2, CO, CH_4, C_2H_6	no	[1]
DGER-MPDA	CH_3CHO, H_2O, resorcinol, decomposed aromatic compounds	CH_3CHO, H_2O, H, CH_4, HC≡N, CH≡CH	no	[2]
Poly-*m*-phenylene-isophthalamide (PMPIA) (nomex, phenylon); poly-*p*-phenylene-terephthalamide (PPTA) (kevlar, arenka); poly-*p*-benzamide; poly-amidebenzimidazole (PABI)	NH_3, H_2O, CO, CO_2, 	NH_3, H_2O, CO, CO_2	no	[3]

underlying the thermofluctuation concept. If the treatment is restricted to the investigation of the mechanodegradation of a macromolecule only within the framework of classical mechanics, then one can expect that the method of molecular dynamics (MD) will prove most compatible with the significantly non-linear character of the mechanodegradation process and will be most effective in the given instance.

At the present time, this method has been developing vigorously on the basis of modern computer techniques. With the aid of the MD method, it is possible to investigate in detail the molecular dynamics of various processes in the time range 10^{-14}–10^{-11} s.

Table 2. High-energy molecular products of the mechanodegradation of polymeric materials.[5]

Polymer	Products	V, m s^{-1}	E_{trans}, eV	T_{tr}, K
PMMA	MMA	1160^{+160}	$0.70^{+0.21}$	5410^{+1530}
	H_2O	1580^{+335}	$0.23^{+0.11}$	2190^{+460}
DGER–MPDA	CH_3CHO	1210^{+100}	$0.33^{+0.06}$	2570^{+450}
	H_2O	1680^{+305}_{-100}	$0.26^{+0.11}_{-0.03}$	2040^{+810}_{-280}
Ebonite	H_2O	1690	27	2065

Note. V is the velocity of the translational motion of the moelcules, $E_{trans} = mV^2/2$ the kinetic energy of the translational motion of the molecules, T_{tr} the translational temperature [the experimental errors ($\pm$), determined by the accuracy of the method, are indicated for V, E_{trans}, and T_{tr}].

II. The application of the method of molecular dynamics

1. Mechanodegradation

The decomposition of an extended chain of atoms was investigated by the MD method for the first time by Toda et al.[7] on a one-dimensional model. The interaction between neighbouring atoms was specified by a potential of a special type:

$$\Phi(r) = \begin{cases} e^{-r} + r + \text{const}, & r < r_{cr} \\ \text{const}, & r > r_{cr}, \end{cases}$$

since simple analytical solutions of the equations of motion $f_n = \Omega^2 \operatorname{sech}^2(kn \pm \Omega t)$, where f_n is the force of the compression of the nth bond, $\Omega = m^{-1/2} \sin nk$, r is the deviation of the position of the atom from equilibrium (bond deformation), m the mass of the atom, k a constant, and t the time, are known for a chain with such a potential. These solutions represent unified compression waves (solitons) propagated along the chain of atoms.

The following sequence of events after the rupture of a uniformly extended chain has been noted:[7] (1) immediately after rupture, a wave of stresses is generated and is propagated in the direction towards the fixed end; (2) after reflection from the latter, the wave is transformed into a sequence of compression pulses (solitons); (3) each soliton reaching the free end of the chain leads to the extension of the extreme bond, which exceeds by several per cent the initial extension r_{init}. However, since the critical stretching deformation of the bond r_{cr} was always specified by the authors[7] in the range $(1.015–1.07)r_{init}$, then such extension always leads to the abstraction of the extreme atom of the chain. Thus, in the initial degradation stage consecutive removal of atoms from the free end takes place and is followed by random breaks of the chain in different places. The above degradation sequence holds for a wide range of initial extensions of the chain.

The fragmentation of a uniformly extended one-dimensional chain of atoms has also been studied by the MD method in other investigations.[8,9] In contrast to Toda, Mel'ker et al.[8] and Grigoryan et al.[9] used the Morse potential for the description of the interaction between neighbouring atoms of the chain. The generation of large-amplitude compression pulses on reflection of the relaxation wave from the fixed end, analogous to those observed by Toda,[7] was noted. However, in contrast to Toda's work,[7] the rupture of the extreme bond was not observed on reflection of the compression pulses from the free end despite the fact that the stretching deformation exceeded ε_{cr}.† The kinetic energy of the motion of the centres of mass of the fragments was considerable and amounted to 25% of the total energy of the system. The deformation of the individual bonds in the fragments reached $2.2\varepsilon_{cr}$ although further fragmentation was not observed.

The occurrence of low-frequency vibrations in the extended chain has been noted by Mel'ker and Kuznetsova,[10] which the authors attribute to the "two-well nature" of the potential for any internal chain atom.[11] The two-well form of the potential is responsible for the existence of stable lengthened bonds capable of migrating. It has been suggested[10] that they be referred to as quasi-particles—dilatons, and the dissociation of an extended chain has been interpreted[12] as a result of the merging of dilatons.

A series of studies by Mel'ker and co-workers has been devoted to the mechanism of the dissociation of an interatomic bond in an extended chain of atoms.[13–15] Two types of ruptures are distinguished. The first type of rupture—the single-step rupture—is associated with the generation of a dissociative energy fluctuation embracing approximately 10 atoms. In the region of the fluctuation, the deformation of the interatomic bonds exceeds the average value and the motion of the atoms is correlated.[13] In rupture, the energy of the fluctuation is concentrated on one bond, which is rapidly and monotonically lengthened up to dissociation. This type of rupture is characteristic of a relatively high energy density in the deformed chain of atoms, when its lifetime does not exceed 10^3 periods of the atomic vibrations. The second type of rupture of the interatomic bond—the two-step rupture, whose probability increases with decrease in the energy density in the chain, has been noted by Mikhailin and Mel'ker.[14,15] The interatomic bond is rapidly lengthened up to values in the range $\varepsilon = (2–4)\varepsilon_{cr}$ and oscillates about the level attained over a period $(2–7)\tau_0$. The bond dissociation is then rapidly completed.

The longevity of the polymer chain under load at a specified temperature has been investigated by Zaitsev and Razumovskaya.[16] A one-dimensional chain of atoms, whose interaction is described by the Morse potential, was used as the model. The appearance of two compression regions (lattice solitons), diverging from the site of chain rupture at ultrasonic velocities, was noted.

†The bond deformation $\varepsilon \equiv (r - r_0)/r_0$, where r is the distance between the atoms and r_0 its equilibrium value. The critical bond formation $\varepsilon_{cr} = \ln 2/\alpha r_0$ corresponds to the ultimate strength of the interatomic bond $F_m = \alpha U_0/2$, where α and U_0 are parameters of the Morse potential.

Taking into account the fact that the principal characteristics of the mechanodegradation of the polymer chain are determined by the strong anharmonicity of the vibrational-wave excitations, arising during the different stages, it is useful to analyse the instances of intense shock interaction of polyatomic systems in which anharmonicity plays a decisive role.

2. Shock waves

A study by Bettech and Powell was devoted to the numerical modelling of the propagation of a shock wave in a one-dimensional chain.[17] The investigation established that the development of the process involving the oscillation of particles behind the shock wave front is determined in the early stage by the dispersion, after which non-linear effects become increasingly more significant. During the propagation of a shock wave, decaying oscillations are converted into a sequence of distinct pulses—solitons (Fig.1*a*). The stability of solitons (*A*, *B*, *C*) in relation to collisions and the thermal background (Fig.1*b*) leads to the absence of a tendency towards the "disordering" of the energy, i.e. towards the attainment of thermal equilibrium. The energy is not thermalised behind the shock wave front and hence the temperature does not increase.

The propagation of a shock wave in an iron crystal has been investigated by Walker et al.[18] The behaviour of impurity diatomic molecular H_2 and C–H species (probes) in the three-dimensional iron lattice during the passage of the shock wave front was investigated by the MD method. Figs.2 and 3 illustrate the time variation of the translational (*a*), rotational (*b*) and vibrational (*c*) energies of the H_2 and C–H probe molecules respectively as well as the disposition of the iron atoms and probe molecules in the system before the impacts (*d*) of the plate against the block and at the instant corresponding to 40 time units (1 time unit = 10^{-14} s) (*e*) corresponding to the attainment of the end of the block by the shock wave. The iron

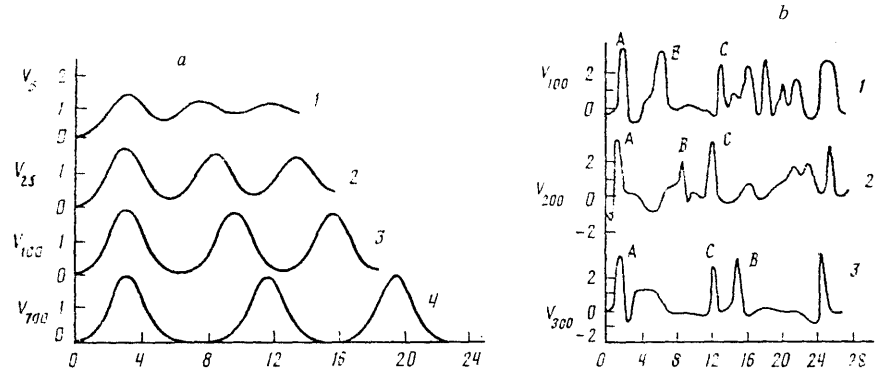


Figure 1. Variation with time τ of the velocities V of different particles (5th, 25th, 100th, and 700th) in the chain:[17] *a*) initially unperturbed; *b*) at a non-zero initial temperature; τ_0 (arbitrary units)—the instant when each particle is acted upon by the shock wave: *a*: *1*) τ_0 = 5.6; *2*) τ_0 = 36.5; *3*) τ_0 = 148.9; *4*) τ_0 = 1041.0; *b*: *1*) τ_0 = 73; *2*) τ_0 = 140; *3*) τ_0 = 209.

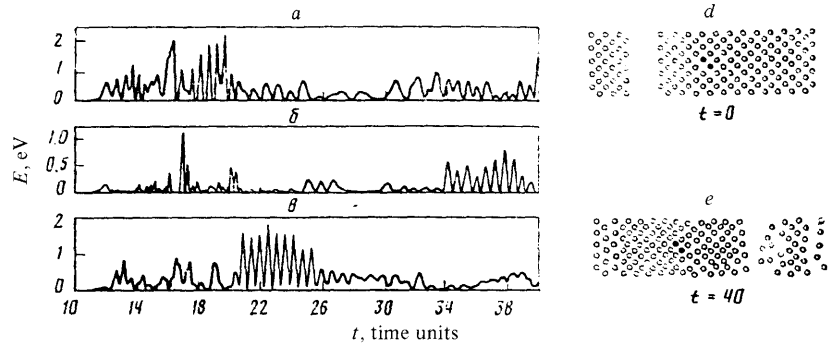


Figure 2. Time variation of the energy E [*a*) translational; *b*) rotational; *c*) vibrational] of the H_2 probe molecule in the Fe lattice during the passage of the shock wave front; *d*) disposition of atoms in the system before impact; *e*) instantaneous disposition of atoms in the system after 40 time units have elapsed (1 unit = 10^{-14} s) corresponding to the shock wave reaching the end of the block; Fe atoms are represented by open circles and the atoms of the H_2 probe molecule by filled circles.[18]

atoms are represented by circles and the atoms of the probe molecules are represented by points. Figs.2 and 3 show that the variation of the kinetic energy of the translational motion of the diatomic probe molecules reaches 6 eV and has the form of a sequence of unified brief ($\sim 10^{-14}$ s) pulses resembling solitons. The changes in the energies of rotational and vibrational motions (b) and (c), reaching several eV, have a similar form. Such large energies of the vibrational motion lead to the dissociation of molecules: for a short period if the molecule is in a 'cage' and irreversibly if the molecule is at the boundary of the free volume.

3. Elementary thermal excitations

In his analysis by means of the procedure described by Battech and Powell[17] of the thermal vibrations in a one-dimensional chain of 500 atoms, whose interaction is described by the Morse potential, Zhukov[19] showed that two types of lattice excitations coexist in the thermalised chain: solitons and phonons. The solitons are in fact the high energy carriers and their contribution to the overall thermal energy of the thermalised lattice amounts to tens per cent and increases with increase in temperature. Fig.4 illustrates the instantaneous velocities of the atoms in the middle part of a 500-atom chain. In the initial instant (*a*), only a small zone in the centre of the chain comprising 20 atoms (from the 250th to the 270th) is heated and the rest of the chain is "cold". The migration of energy from "hot" to the "cold" zone is effected both by phonons and solitons. However, since the velocity of the soliton is greater than the velocity of sound, the solitons emerge from the heated zone, overtaking the phonons. Figs.4*b* and 4*c* illustrate the instantaneous velocities of atoms after 2000 and 4000 time steps respectively and the solitons which have emerged are designated by vertical arrows.

The occurrence of stable elementary excitations of the soliton type in a chain of atoms fixed at the edges, whose interaction is described by the Morse potential, has been demonstrated analytically by Collins[20] and numerically by Rolfe et al.[21] Rolfe et al.[21] not only demonstrated the possibility of the existence of solitons in one-dimensional chains with different interatomic interaction potentials (Morse, Lennard-Jones 6–12 and 16–32) but also established that the reflection of the solitons from the fixed and free ends as well as the collision of the solitons with one another are similar to the behaviour of solitons in a Toda chain for all the potentials examined.

The appearance of such excitations in the mechanodegradation of a uniformly extended one-dimensional chain of Morse oscillators and the interaction of solitons having different energies with the extended chain have been described.[22,23] In addition, a study has been made[22] of the dependence of the mass spectrum of the mechanodegradation products on the length and degree of extension of the chain.

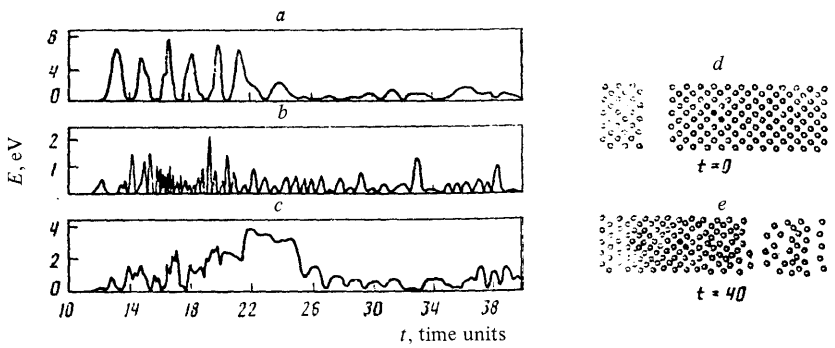


Figure 3. See the caption to Fig. 2; C–H molecular probe in the Fe lattice.[18]

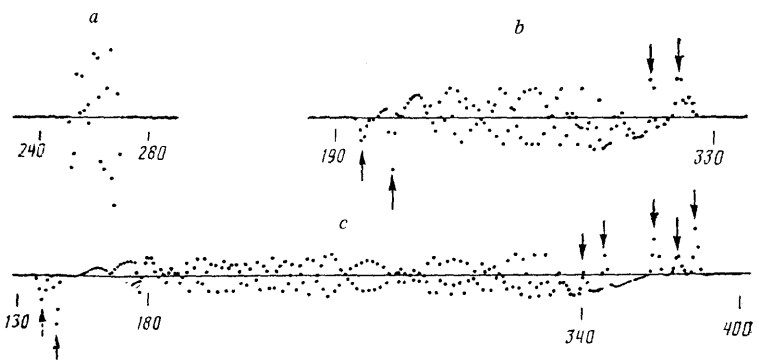


Figure 4. Instantaneous velocities of the atoms in the chain: *a*) in the initial instant; *b*) after 2000 time steps; *c*) after 4000 time steps;[19] the numerals denote the numbering of the atoms.

In his study of the properties of the elementary thermal excitations in a strongly heated chain of atoms, whose interaction is described by the Lennard-Jones potential, Lagunov[24] established that, as in the case of the Morse potential, they are equivalent to the lattice solitons existing in the Toda chain.[25] On the basis of this conclusion, he examined[24] the thermal fluctuation-induced dissociation of a uniformly extended chain either as a result of the interaction of countercurrent streams of solitons and antisolitons or as a result of the interaction of dilatons with antidilatons. It is suggested that the large-scale regions between the centres of solitons, migrating together with them, rather than the highly extended chain as in the study of Mel'ker et al.,[12] be regarded as dilatons functioning as elementary carriers of the stretching deformation. Lagunov[24] analysed the dissociation step solely in "dilaton" and "antidilaton" terms, referring, however, to the dissociation mechanism itself as a "soliton" mechanism. Furthermore, he noted[24] that a pair comprising a kink and an antikink (i.e. a pair of solitions of the topological type) diverge from the rupture site, which leads to a gradual relaxation of the chain.

Unfortunately, on the basis of the individual experimental[1-5] and theoretical[7-24] results available at present in the field of the mechanodegradation of polymers, it is impossible to achieve a clear understanding of the mechanism of this process. The theoretical results of different workers are contradictory and unrelated to the available experimental data. However, one should note that the intense anharmonic excitations resembling solitons observed by different workers undoubtedly play an important role. This complex situation in the mechanodegradation of polymers, which has a great practical importance, has led the present authors to carry out a more detailed investigation of this process.[26,27]

The stretching (as far as rupture) and subsequent mechanodegradation of a continuous polymer chain in an amorphous layer of a linearly oriented polymer with a fibrillar structure was investigated by the method of molecular dynamics. One-dimensional chains made up of 50 and 100 atoms were chosen as the object of study. The masses of all the atoms were the same and equal to that of the carbon atom (2×10^{-23} g). The interatomic interaction was described by the Morse potential with the parameters characteristic of the C–C bond in polyethylene. Account was taken only of the interaction between nearest neighbour atoms. For the numerical solution of the system of differential equations of motion of the chain atoms, the RKF 45 program[28] was used with the automatic selection of the integration step, based on the modified fourth–fifth order Runge-Kutta method. In order to avoid the unjustified decrease in the step after the sharp cut-off of the potential, a "smooth" cut-off was achieved with the aid of a cubic polynomial. Thus the potential employed had the form

$$U(r) = \begin{cases} D\left[e^{-2b(r-r_0)} - 2e^{-b(r-r_0)}\right], & r \leqslant r_1, \\ C_1(r-r_2)^2 + C_2(r-r_2)^3, & r_1 \leqslant r \leqslant r_2, \\ 0, & r_2 \leqslant r. \end{cases}$$

The parameters of the Morse potential were $D = 3.5$ eV, $b = 2$ Å^{-1}, and $r_0 = 1.54$ Å.

The constants C_1 and C_2 were selected on the basis of the condition of the continuity of the potential and of its first derivative at the point r_1.

At the initial instant, the distances between neighbouring atoms are r_0 and the velocities of all the atoms are zero (the chain is at the temperature 0 K). The first atom is fixed so that it is immobile. The extension of the chain was specified by the movement of the last atom in the positive direction at a constant velocity V. The calculations were performed for two rates of stretching: $V = 0.1V_{so}$ and $V = 0.05V_{so}$, where $V_{so} = r_0 b(2D/m)^{1/2} = 23.08 \times 10^3$ m s$^{-1} \simeq$ 231 Å ps^{-1} is the velocity of sound. The stretching of chains at such high rates takes place at the apex of a major crack at the concluding stage of its growth at a rate close to the velocity of sound. In an experimental study of precisely this stage of the rupture process,[5] it was possible to detect high-energy molecular products of the mechanodegradation of polymers (Table 2).

The time used to observe the trajectories of the motion of atoms was 3.5–7 ps.

III. Characteristic features of the mechanodegradation of polymer chains

1. The mechanisms of the ruptures

We shall consider the principal characteristics of the mechanodegradation in relation to a 50-atom chain stretched at a rate of 23 Å ps^{-1} $\simeq 0.1V_{so}$. In the initial instant, the velocities of all the atoms are zero, i.e. the chain is at the temperature 0 K.

Fig.5 presents the trajectories of the motion of all the 50 chain atoms. The coordinates $X_i(t)$ (i = 1–50) of all the atoms (in Å) are plotted along the left-hand ordinate axis and the time t [in time units (1 time unit = 10^{-14} s)] is plotted on the abscissa axis. Scale divisions, in steps of 1 Å are indicated on the right-hand ordinate axis to facilitate analysis of the process. The upper straight line represents the trajectory of the motion of the last (51st) atom at a constant velocity $V_{51} = 23$ Å ps^{-1}. The figure clearly shows the sites and instants of all the ruptures. Certain ruptures are "healed", i.e. recombination takes place, which is associated with the presence of two boundaries, one stationary and one moving at a constant velocity, which prevent the free movement of the degradation products by virtue of the one-dimensional nature of the model. It can be assumed that the first four breaks, indicated in the figure by filled circles, occurred without being influenced by the boundaries (if one disregards the reflection from the stationary boundary of the extension wave, which initiates the first chain rupture, as will be shown below). The first stage of the chain extension process is fully determined by the propagation of the extension wave (Fig.6). Each curve represents the distribution of the bond deformations along the chain at a fixed instant. The numbers of the bonds are plotted along the abscissa axis and the number of the curve is plotted on the left-hand side ordinate axis (the position of the number on the ordinate axis specifies the zero deformation level for the corresponding curve). On the left, the time (in time units) elapsed from the instant of the start of the extension is indicated above each curve and the deformation scale (in 10^{-1} Å) is indicated on the right-hand ordinate axis. The extension wave is propagated along the chain from right to left, i.e. from the extreme (51st) atom, moving at a constant velocity, to the fixed end. The velocity of the potential wave front is 245 Å ps^{-1}, which is close to the velocity of sound calculated from the formula $V_{so} = r_0 b(2D/m)^{1/2} \simeq 231$ Å ps^{-1}.

By virtue of the dispersion of the system considered, decaying atomic vibrations, also propagated along the chain in the form of a wave, are observed behind the wave front. However, the vibration wave is propagated along a chain which has already been stretched (whose effective force constants are smaller than those of the unstretched chain) and its velocity is therefore lower than that of sound. This factor leads to the "spreading" of the extension wave front. At the instant corresponding to 31 time units, the front

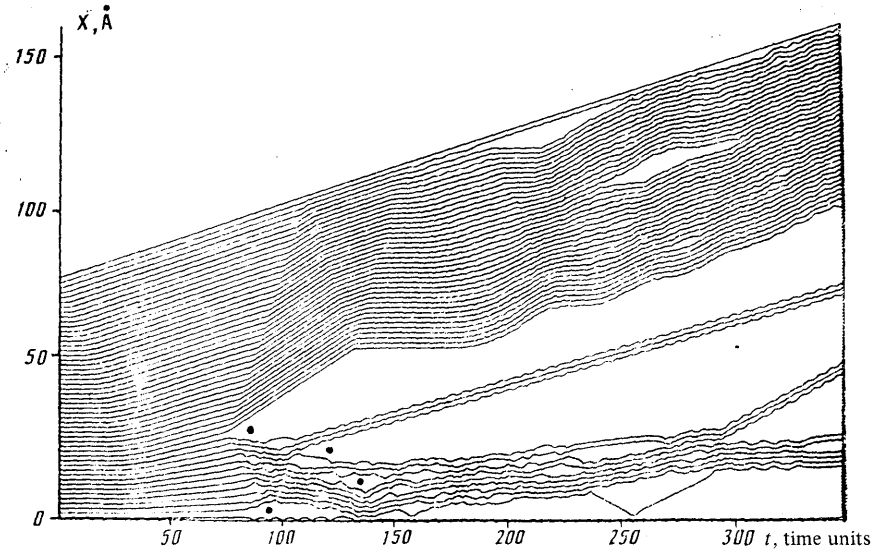


Figure 5. Time variation of the coordinates of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$;[27] in the initial instant, the chain temperature is 0 K.

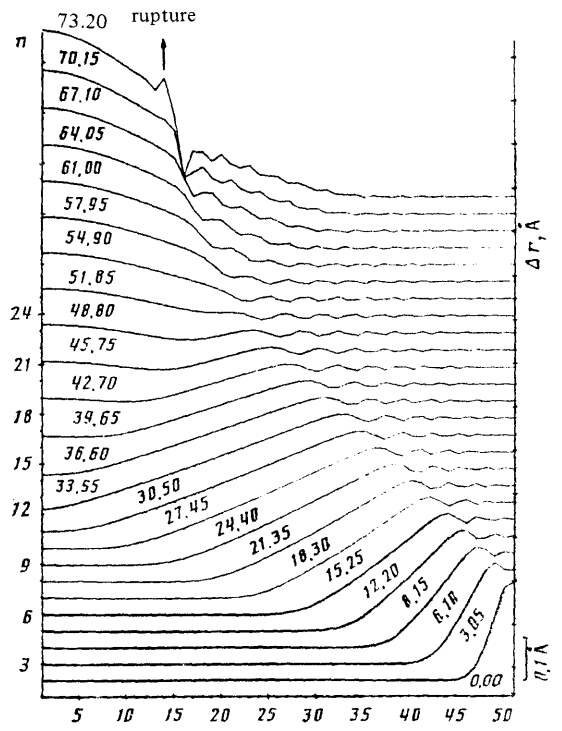


Figure 6. Time variation of the distribution of the bond deformations $\Delta r \equiv r - r_0$ along the chain from the initial instant up to the instant of the first rupture;[27] i = number of the bond; n = number of the atom.

reaches the fixed end and is reflected from it in the form of a high-amplitude wave. From this instant, the high-amplitude extension wave is propagated towards the vibration wave. Collision of these two waves occurs at time $t \simeq 50$ time units in the 22nd bond. The velocity of the vibration wave then diminishes as it passes to the increasingly stretched regions of the extension wave front. When the vibration wave front reaches the region with the deformation $\varepsilon > \varepsilon_{cr} = 0.224$, the chain ruptures (in the given instance, the 14th bond is ruptured).

Thus the mechanism of the first rupture of the "cold" chain stretched at a rate $V = 0.1V_{so}$ is due to the collision of the dispersion vibration wave with the extension wave moving in opposition to it, the rupture step itself occurring at the site where the following two conditions are satisfied simultaneously at the instant of the arrival of the first vibration: $\varepsilon > \varepsilon_{cr}$ and $\dot{\varepsilon} > 0$.

At the instant of rupture (73 time units), the propagation of the deformation along the chain is significantly non-uniform: $\varepsilon > \varepsilon_{cr}$ for bonds 1–14 and $\varepsilon < \varepsilon_{cr}$ for bonds 15–50. The forms of the relaxation waves propagated from the rupture site are therefore different in the chain fragments 1–13 and 14–51 (Fig.7). The relaxation wave front in the fragment 1–13 ($\varepsilon > \varepsilon_{cr}$) represents a kink (a topological soliton) and that in the fragment 14–51 is a lattice soliton. The propagation of kinks from the rupture site has also been noted by Grigoryan et al.[23]

For a slower ($V_{ext} = 0.05V_{so}$) extension of the cold chain, a different rupture mechanism, associated with a structural transition in the most stretched part of the chain, is observed. When the stretching deformation reaches $\varepsilon_{cr} = 0.224$, there is an abrupt transition of the chain atoms to a new state of equilibrium. The chain structure then changes in such a way that, instead of uniformly extended bonds, a sequence of long (L) and normal (N) bonds alternating along the chain arises: ...LNLNLNLN...

The length of the L-bond is $l_L \simeq r_0 + 2\varepsilon_{cr}r_0 = (1 + 2\varepsilon_{cr})r_0$, where $\varepsilon_{cr} \simeq 0.224$, while the length of the N-bond is $l_N \simeq r_0$. This structural transition is associated with the fact that, when the stretching deformation reaches the critical value ε_{cr}, there is a qualitative change in the form of the effective potential for each internal chain atom: the potential changes from the one-well type to the two-well type. A similar change in the form of the potential for an internal atom of the chain when the latter was stretched was investigated previously by Mel'ker and Kusnetsova.[11] Fig.8 shows how the form of the potential for an internal atom in a three-atom one-dimensional system changes when the extreme atoms move apart by 0.3, 0.5, and 0.7 Å. Evidently the transition from the one-well to the two-well potential takes place for stretching deformations in the range 0.3 to 0.5 Å.

Figs.9 and 10 illustrate the slow extension of a 50-atom chain in which a structural transition, terminating in two chain ruptures, takes place over a long segment. Fig.9 illustrates the trajectories of the motion of all the 50 atoms. The numbers of the atoms are

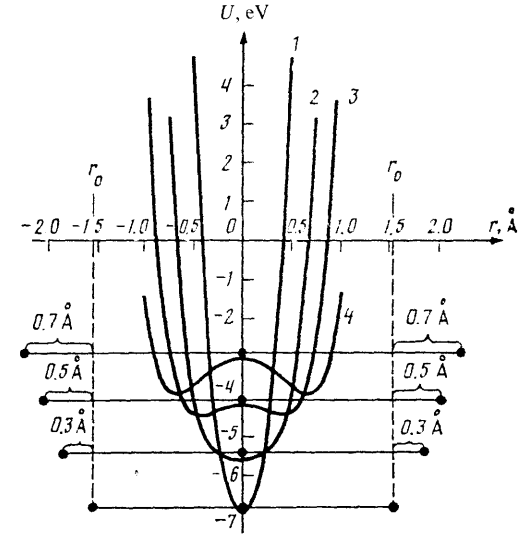


Figure 8. The change in the form of the potential for an internal atom of the chain on extension of the latter; $\Delta r \equiv r - r_0$ (Å): *1*) 0; *2*) 0.3; *3*) 0.5; *4*) 0.7.[27]

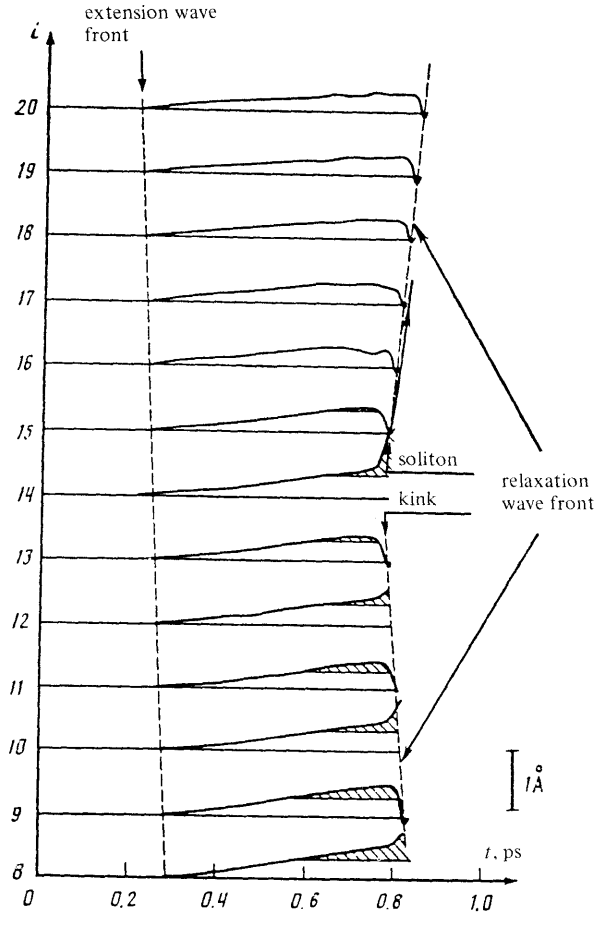


Figure 7. Time variation of the bond deformations in the vicinity of the first rupture; qualitative difference between the relaxation waves propagated at the site of the first rupture in the highly stretched ($\varepsilon > \varepsilon_{cr}$) fragment 1–13 and in the slightly stretched ($\varepsilon < \varepsilon_{cr}$) fragment 14–51;[27] i = number of the bond.

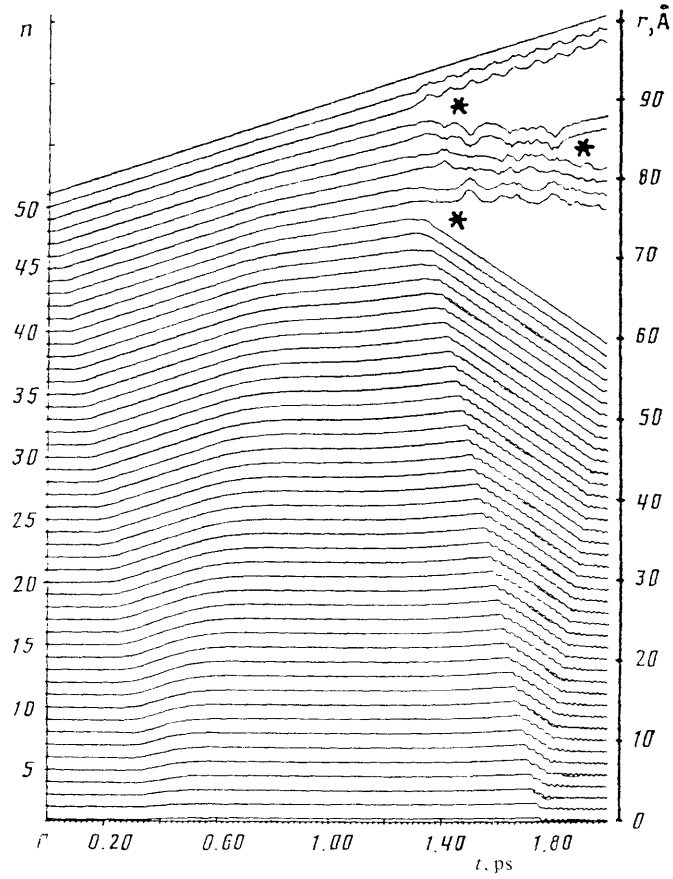


Figure 9. The trajectories of the motion of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.05V_{so}$. The ruptures are designated by an asterisk (*);[27] n = the number of the atom; t = time; r = atomic coordinate.

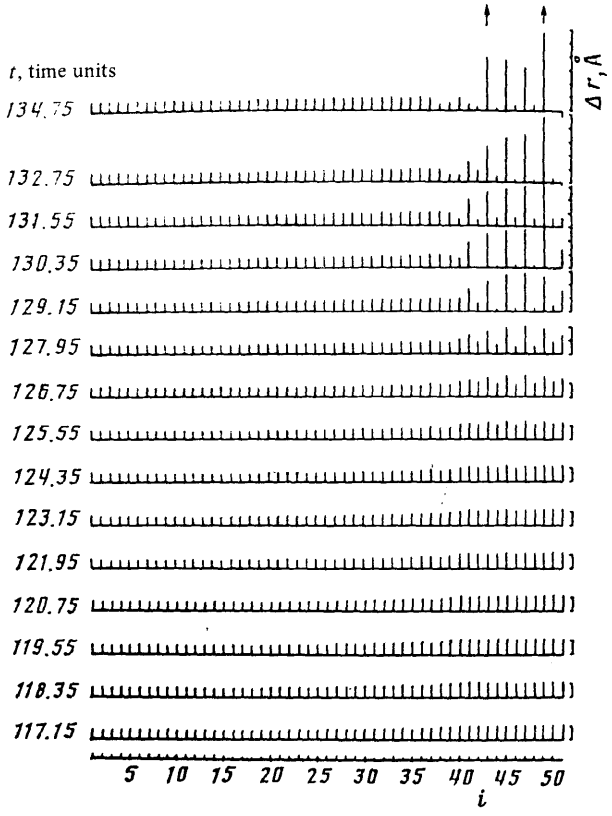


Figure 10. The structural transition in a 50-atom chain stretched at the rate $V_{str} = 0.05V_{so}$ in the pre-rupture stage:[27] i = the number of the bond in the chain; $\Delta r \equiv r - r_0$ the stretching deformation in Å; 1 division = 0.3 Å; t = time expressed in time units (1 time unit = 10^{-14} s).

plotted on the left-hand ordinate axis, the atomic coordinates (r) (in Å) are plotted on the right-hand ordinate axis, and the times (in ps) are plotted on the abscissa. In the time interval 1.20–1.35 ps in the section between the 40th and 50th atom, the critical stretching deformation $\varepsilon_{cr} = 0.224$ is attained and leads to a structural transition with subsequent ruptures of the 43rd and 49th bonds and the formation of a free 6-atom fragment 43–48. This structural transition in the pre-rupture stage is illustrated in greater detail in Fig.10. The time variation of the deformations of all the chain bonds is illustrated here at intervals of 1.2 time units.

We shall consider the characteristic features of the rapid extension of a polymer chain ($V_{ext} = 0.1V_{so}$). The wave process arising on rapid chain extension leads to a significantly non-uniform distribution of the deformation and energy along the chain. This fact has been disregarded in studies,[7-9,22] devoted to the degradation of "cold" stretched one-dimensional chains. It has been assumed that, at the instant of the first rupture, all the bonds of the chain, except that which is ruptured, are equally stretched. Fig.11 presents the distribution of the potential (curve *1*) and kinetic (curve *2*) energies along the chain at the instant 0.73 ps, i.e. immediately before the first rupture of the 50-atom chain illustrated in Fig.5. The non-uniformity of the energy distribution at the pre-rupture instant is in this case so considerable that significantly different excitation levels are characteristic of the chain fragment formed after the first rupture: thus the energy densities are 1.66 and 0.83 eV/bond in the fragments 1–13 and 14–50 respectively. This fact is responsible not only for the different character of the wave processes in the two fragments (Fig.7) but also leads to more rapid and vigorous degradation of the fragment 1–13 (three ruptures after ~0.5 ps) compared with the slow degradation of the fragment 14–50 (two ruptures after ~3 ps).

We shall now consider the wave processes developing after the first rupture of the chain stretched at a rate $0.1V_{so}$. Fig.12 illustrates the time variation for the kinetic energy of all the chain atoms (see also Fig.5). The numbers of the chain atoms (on the left) and the

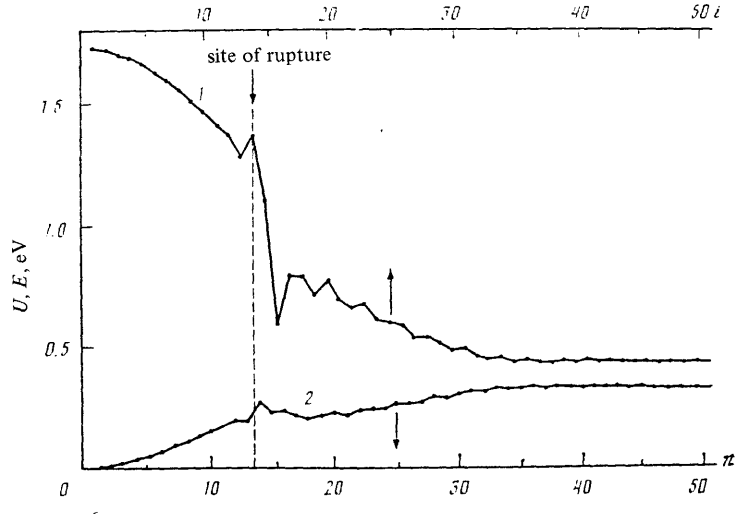


Figure 11. Distribution of the potential energy U (curve *1*) and the kinetic energy E (curve *2*) along the chain at the instant of the first rupture (t = 0.73 ps) of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$;[27] n = number of the atom; i = number of the bond.

kinetic energy scale with 1 division = 1 eV (on the right) are plotted along the ordinate axes and the time (in time units) is plotted along the abscissa axis. As before, the fixed end of the chain is at the lower end of the figure and the end moving at a constant velocity corresponds to the upper part of the figure.

After the first chain rupture (t_1 = 76 time units), individual irregular high-energy (more than 3 eV) localised waves of the type of solitons arise in the fragment 1–13, while a regular sequence of primary solitons, propagated from the site of the first rupture at the upper end of the chain moving at a constant velocity, is formed in the fragment 14–50. On reaching the upper end of the chain, the solitons are reflected and move towards the arriving stream of primary solitons. Interference then occurs between the incoming and reflected streams of solitons, which leads to the amplitude modulation of the soliton sequence. Thus we see that the process developed after the first rupture in both sections of the ruptured chain is quite different from what might have been expected on the basis of the existing ideas about the thermofluctuation character of the degradation process.[6] Instead of the expected conversion of elastic energy into thermal energy and the subsequent appearance of large thermofluctuations under the conditions of random motion, in the initial stages of the degradation process highly ordered modes are observed in the form of localised running waves—solitons. The size of the soliton depends only slightly on the degree of extension (compression) of the part of the chain in which it is located in the given instant and amounts to two–three units. At the instant when the soliton reaches the free end of the chain, its entire energy is converted into the potential energy of the extension of the extreme bond. The energy of the soliton can be determined accurately in this way.

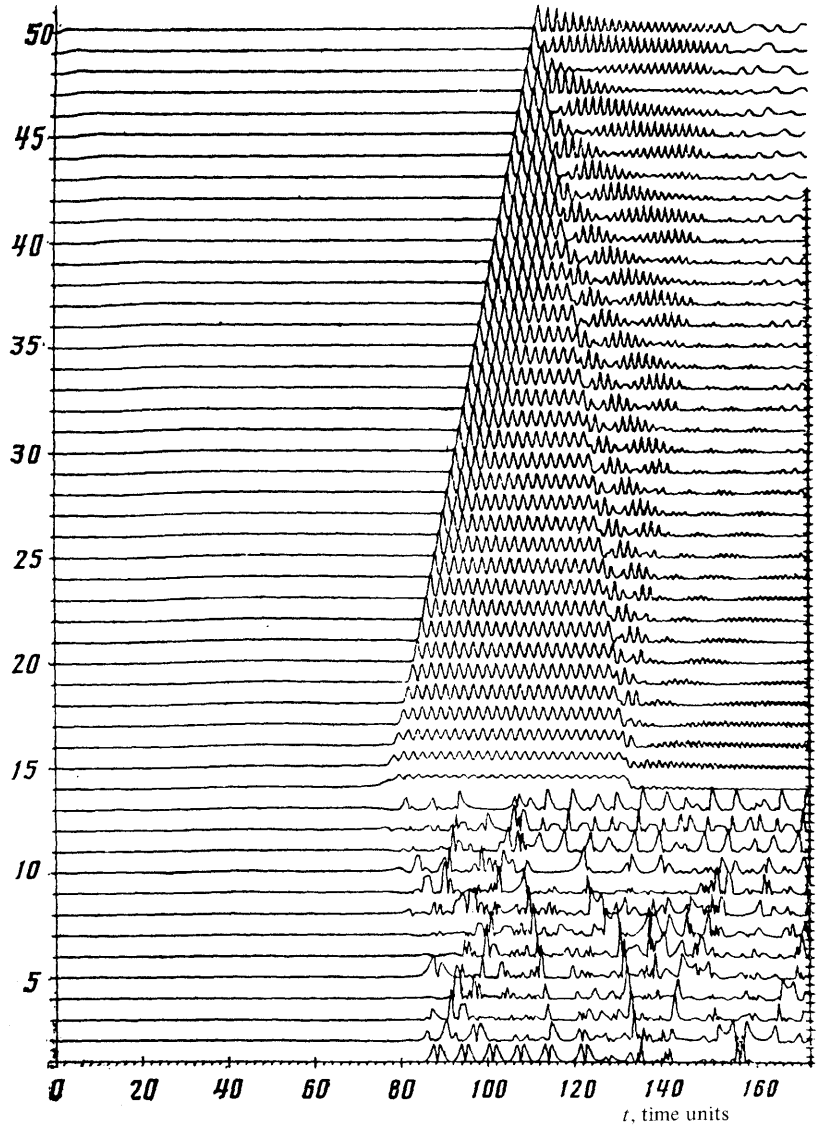


Figure 12. Time variation of the kinetic energy of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$; on the right—1 division = 1 eV; n = the number of the atom; t = time expressed in time units (1 time unit = 10^{-14} s).

By analysing the observed secondary ruptures and then comparing them, it has been possible to identify two most characteristic mechanisms of the rupture processes. The first mechanism, characteristic of the rupture of short fragments (starting from the free ends of larger fragments) is determined by the arrival at the given free end of a packet of solitons moving in one direction. The following feature then holds: the packet, containing N solitons, breaks off a fragment containing N atoms. This mechanism can be briefly formulated as follows: N_{sol} + free end → $N_{atom.fragm.}$. For example, consider the abstraction of the three-atom fragment 20–22 from the 14-atom freely moving fragment 9–22 (Fig.13)—one of the intermediate products of the mechanodegradation of a 100-atom chain. The trajectories of the motion of all the atoms of the freely moving fragment 9–22 are illustrated in Fig.13*a*. At the instant $t \simeq 469$ time units, the 20th bond is ruptured and the three-atom fragment 20–22 is broken off. Fig.13*b* illustrates the time variation of the velocities of all the atoms of the fragment 9–22. The packet of three solitons (numbers *1*, *2*, and *3* in Fig.13*b*), moving from the 9th to the 22nd atom, is clearly seen. Having reached the free end, the first soliton alters sharply the trajectory of the motion of the extreme (22nd) atom. The second soliton, which immediately follows the first, also alters sharply the trajectory of the 21st atom. As a result of this, the diatomic fragment 21–22 begins to separate and the 21st bond is lengthened. Having reached the 20th atom, the somewhat lagging third soliton transfers to this atom its momentum and "throws it over" to the fragment 21–22 being eliminated. As a result the 21st bond is restored and the 20th is lengthened until rupture. In the pre-rupture state ($t \simeq 469$ time units) in the region of the future break, a correlated motion of the atoms in the opposite directions from the site of the future break is observed. The occurrence of the correlated motion of atoms in the pre-rupture instant has been pointed out by Mel'ker and co-workers.[13–15] However, the causes of such correlated motion of atoms were not considered. We suggested that such a cause is the movement of the packets of solitons *1–3* and *4–6* towards each other (Fig.3*b*), resulting in rupture. The size of the packet of solitons determines the size of the region of the correlated motion of atoms.

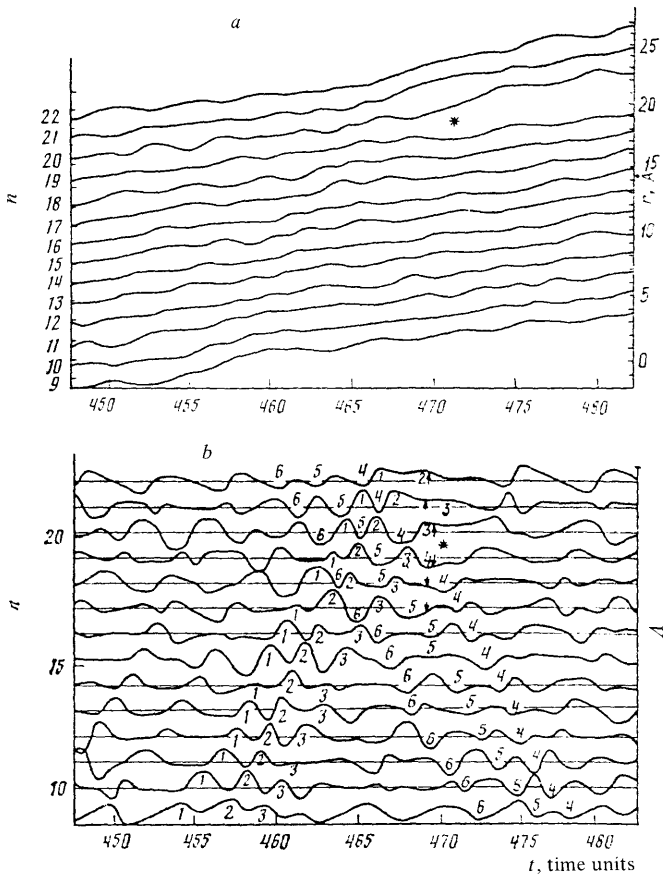


Figure 13. The abstraction of a three-atom fragment by a three-solition packet: *a*) trajectories of the motion of the atoms in the dissociating fragment 9–22; *b*) time variation of the velocities of the atoms in the dissociating fragment 9–22;[27] n = number of the atom; r = atomic coordinate in Å (1 division = 1 Å); V = velocity of the atom (arbitrary units); t = time expressed in time units.

The second rupture mechanism involves the entry of a soliton into the stretching region of the chain, i.e. into the zone for which the following two conditions are fulfilled simultaneously: $\varepsilon > \varepsilon_{cr}$ and $\varepsilon > 0$. This mechanism is similar to the mechanism of the first rupture considered above (Fig.6) and therefore does not require special illustrations.

2. The formation of C = C double bonds and excited products

In the intense excitation of the chain observed after its first rupture, there is a possibility of the formation of multiple bonds (C = C double bonds and even C ≡ C triple bonds) together with degradation. Since a soliton is a zone of compressed bonds and at the same time a zone with a high kinetic energy (momentum), the movement of high-energy (1–3 eV) solitons entails the compression of bonds to lengths equal to and even smaller than the length of the C = C double bond and the simultaneous transfer of momentum to the lateral atoms sufficient to break them off. The time variation of only those compressive deformations which exceed 0.2 Å, which correspond to the formation of a C = C double bond, is illustrated in Fig.14 for the first molecular product (2–13) of the mechanodegradation of a 50-atom chain (the stretching and degradation are illustrated in Fig.5). It is seen from Fig.14 that, even after the very short lifetime of the free fragment, all its bonds undergo repeatedly strong compressions under the influence of the high-energy solitons. Thus one may expect that the propagation of high-energy solitons in a real macromolecule leads to the formation of C = C double bonds and the "shedding" of side groups. A similar result was obtained in a quantum-mechanical study[29] of the behaviour of terminal alkyl radicals following intense compression of the $C_\alpha - C_\beta$ bond.

Another important result is the formation in the course of the mechanodegradation of the chain of excited low-molecular-weight products with an excess vibrational energy (up to 1.0–1.5 eV/bond) and translational energy E_{trans} (a few eV) (Table 3) which are hence capable of initiating the decomposition of the surrounding polymer chains on collision with the latter. The fact that several "hot", highly excited molecular products, each of which is capable of transmitting excitation and initiating the rupture of one of the neighbouring stressed chains, are formed on rupture and subsequent decomposition of one polymer chain is especially important. Thus there is a possibility of the branching of the mechanodegradation process. Similar considerations have been put forward by Mel'ker and Kuznetsova.[8]

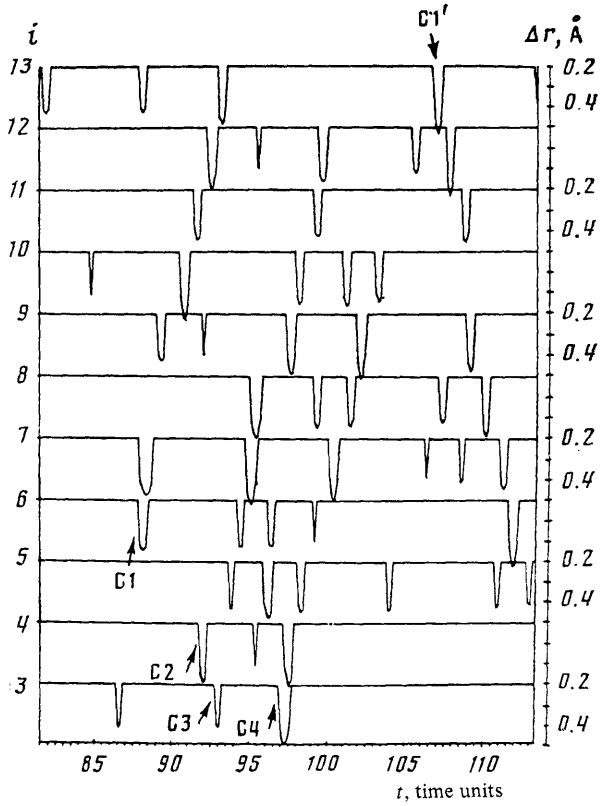


Figure 14. Compression of the C–C bonds by high-energy solitons (~3 eV) to lengths less than the length of the C = C double bond;[27] Δr = compressive deformation (in Å) exceeding 0.2 Å (1 division = 1 Å); C1, C2, C3, C4, and C1′ = high-energy solitons; i = number of the bond; t = time expressed in time units (1 time unit = 10^{-14} s).

Table 3. Information about the molecular products of the mechanodegradation of chains at 0 K.

N	V_{str}	Initial position of fragment in chain	τ, time units	n'	E_{trans}, eV	E_{vibr}, eV	$E_{vibr}/(n'-1)$, eV
50	$0.1V_{so}$	2—13	93.977	12	0.001	17.364	1.58
		11—13	119.25	3	**0.764**	2.024	1.01
		8—10	136.971	3	0.001	3.261	1.63
50	$0.05V_{so}$	43—48	148.881	6	0.516	5.20	1.04
		43—46	201.026	4	**0.656**	1.438	0.48
		47—48	201.026	2	0.028	0.096	0.096
100	$0.1V_{so}$	10—27	157.741	18	0.016	21.40	1.26
		5—27	180.691	23	0.040	20.97	0.95
		5—22	182.579	18	0.312	13.52	0.80
		23—27	182.579	5	**2.22**	1.07	0.27
		15—22	217.149	8	0.295	7.49	1.07
		19—22	307.930	4	0.259	2.20	0.73

Note. N is the number of atoms in the chain, V_{str} the rate of stretching of the chain, τ the instant of the formation of the product, n' the number of atoms in the product, E_{trans} the kinetic energy of the translational motion of the product, E_{vibr} the vibrational energy of the product, $n'-1$ the number of bonds in the product, and $E_{vibr}/(n'-1)$ the density of the vibrational energy in the product.

The proposed branched chain mechanism of the breakdown of polymer chains can explain the known explosive character of the formation of submicrocracks and microcracks.

3. The energetics of the mechanodegradation process

In order to determine the mechanodegradation yields, we shall consider the energetics of the entire process. The energy balance will be expressed by the equation

$$U_0 = nD + \sum_{i=2}^{n-1} E_i + E_1 + E_n,$$

where U_0 is the elastic (potential) energy stored in the initial polymer chain at the instant of the first rupture, n the number of ruptures, D the C–C bond dissociation energy, E_i the total energy of the ith molecular product ($E_i = E_{vibr} + E_{trans}$), and E_1 and E_n are the total energies of the two ends of the chain remaining after mechanodegradation and linked to the polymer matrix.

The first term (nD) on the right-hand side of the equation represents the "pure" energy expenditure on the mechanodegradation. We shall call the ratio nD/U_0 the energy yield of the mechanodegradation and shall designate it by the letter Y. We also introduce the following quantities: the yield of mechanodegradation in terms of ruptures Y', defined as the number of ruptures per 10 eV of the stored elastic energy, and the yield of the mechanodegradation in terms of molecular products Y'', defined as the amount of molecular products formed as a result of the mechanodegradation per 10 eV of the stored elastic energy.

The quantities Y' and Y'' were introduced because they can be determined in a physical experiment, for example, by EPR, IR spectroscopy, and mass spectrometry, and can be compared with the results of numerical modelling. Table 4 presents the yields Y, Y', and Y'' for the case investigated.

Table 4. The mechanodegradation yields.

N	V_{str}, Å ps^{-1}	U_0, eV	n	Y	Y', $n/(10$ eV)	$n-1$	Y'', $(n-1)/(10$ eV)
50	23	42.5	3	0.247	0.7	2	0.47
50	11.5	30.0	3	0.350	1.0	2	0.66
100	23	76.0	4	0.184	0.5	3	0.40

Note. T = 0 K, U_0 is the potential energy stored in the chain at the instant of the first rupture, and $n-1$ is the number of products.

The energy of the molecular mechanodegradation products

$$\left(\text{the sum } E_1 + \sum_{i=2}^{n-1} E_i + E_n\right)$$

over a period of ~10^{-12} s is transmitted to the macromolecules nearest to the rupture site and then spreads into the bulk of the polymer already in the form of waves of the type of solitons. The high stability of solitons suggests that the scattering of their energy requires an appreciable number of scattering centres, as a result of which the energy of the relaxation wave is thermalised over a large ensemble of atoms and the heating of the polymer in the vicinity of the rupture is therefore insufficient for the occurrence of secondary thermal degradation reactions. This factor is apparently the cause of

the difference between the compositions of the molecular products of thermal degradation of mechanodegradation, established experimentally by different investigators for different polymers (Table 1).

IV. Principal results and prospects

The study of the mechanodegradation of a one-dimensional model of a polymer chain by the method of molecular dynamics and analysis of the results in terms of the theory of non-linear waves have shown that unified non-linear waves of the type of solitons, which are the only high-energy agents in the process, play a decisive role in mechanodegradation. For a long time (~ 10 ps) after the rupture of the stretched chain, there is no significant thermalisation of the elastic energy stored in it and no thermofluctuations are observed in the generally accepted sense.[6] The high-energy molecular mechanodegradation products observed experimentally by Enikolopian et al.[5] are formed only in the initial stage of the degradation of the polymer chain over a time range 10^{-2}–1 ps after its first rupture.

Comparative analysis of all the observed ruptures established that the ruptures occur via three main mechanisms. The first mechanism, characteristic solely of primary ruptures, involves a structural transition in the most stretched section of the polymer chain. The second mechanism, characteristic solely of secondary ruptures in the initial stage of the mechanodegradation in those sections of the polymer chain where the energy density is very high (~ 1 eV/unit), is determined by the arrival at the free end of the chain (or a large fragment) of a packet of N solitons moving in one direction. The following feature has been established: a packet of N solitons breaks off a fragment containing N atoms. The third mechanism, characteristic of both primary and secondary ruptures in sections of the polymer chain with a low energy density (~ 0.1 eV/unit), involves the entry of a soliton into the stretching region of the chain, i.e. into the zone for which the following two conditions are fulfilled simultaneously: $\varepsilon > \varepsilon_{cr}$ and $\varepsilon > 0$.

It has been shown that high-energy solitons, which are localised compression waves with a high kinetic energy (momentum), can lead to conditions under which there is a possibility of the formation of C = C double bonds and the shedding of lateral atoms. It has been observed that, on rupture of a single chain, there is a possibility of the formation of several high-energy molecular products, each of which is capable of 'damaging' the surrounding polymer chains. Thus the rupture of one chain can be the cause of the branching of the chain process, leading to the explosive formation of submicrocracks and microcracks.

It has been established that an appreciable proportion (tens per cent) of the elastic energy stored in the chain is expended on its degradation.

Despite the satisfactory agreement of the results of MD calculations of the kinetic energy of the translational motion of the moelcular mechanodegradation products (Table 3) and the experimental data (Table 2), further theoretical studies are necessary for the following reasons.

Firstly, the one-dimensional nature of the model precludes the determination of the contribution to the intramolecular dynamics of the deformation of the valence angles and of conformational rearrangements by the motion of lateral atoms and groups and by intermolecular interactions.

Secondly, the "rigid" fixation of the chain at the boundaries leads to its unrealistic isolation. The complete (100%) reflection of the compression and relaxation waves as well as solitons from the boundaries makes the energy level of the entire mechanodegradation process unduly high. A decrease in the influence of the boundaries may be expected in the rupture of "hot" and longer chains.

Thirdly, the consideration of the macromolecules solely in terms of classical mechanics does not permit a direct observation of the quantum-mechanical pathway leading to changes in its structure (for example, hybridisation) under the conditions of high deformations.

In a more complete consideration of the macromolecule as a quantum-mechanical object, it is necessary to take into account the possible conversion of part of the stored energy on extension into the electronic excitation and ionisation energy, which may be observed, as shown by Zarkhin et al.,[30] for considerable deformations of the macromolecule both in the stage involving its extension and after rupture—in the stage of intense intramolecular dynamics.

References

1. V R Regel', O F Pozdynakov, A V Amelin, et al. *Materialy I Vsesoyuznoi Konferentsii po Mass-Spektrometrii* (Proceedings of the Ist All-Union Conference on Mass Spectrometry), Izd. LIYaF, Leningrad, 1972, p. 198
2. L S Zarkhin Abstract of Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1979
3. A E Gal', K E Perepelkin, O F Pozdnyakov, et al. *Preprinty 3-go Mezhdunarodnogo Simpoziuma po Khimicheskim Voloknam* (Preprints of the 3rd International Symposium on Chemical Fibres), Izd. VNIISV, Kalinin, 1981, Vol. 5, p. 69
4. M A Grayson, C J Wolf *Latest Instrumental Methods for the Investigation of the Structure of Polymers* (Edited by J L Koenig) (Translated into Russian), Izd. Mir, Moscow, 1982, pp. 55–88
5. N S Enikolopian, L S Zarkhin, E V Prut *J. Appl. Polym. Sci.*, 1985, **30** 2291
6. V R Regel', A I Slutsker, E E Tomashevskii *Kineticheskaya Priroda Prochnosti Tverdykh Tel* (Kinetic Nature of the Strength of Solids), Izd. Nauka, Moscow, 1974, p. 540
7. M Toda, R Hirota, J Satsuma *Supplement of the Progress of Theoretical Physics*, 1976(59), 148–162
8. A I Mel'ker, A I Mikhailin, T E Kuznetsova *Mekh. Kompoz. Mater.*, 1979(4), 720
9. G A Grigoryan, L S Zarkhin, L I Manevich *Tesizy Dokladov VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel. Tallin* (Abstract of Reports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids, Tallin), Izd. Moskov. Lesotekh. Inst., 1981, p. 80
10. A I Mel'ker, T E Kuznetsova *Fiz. Tverd. Tela*, 1980, **22**(4) 1039
11. A I Mel'ker, T E Kuznetsova *Fiz. Tverd. Tela*, 1977, **19**(8) 1531
12. A I Mel'ker, T E Kuznetsova, A E Vladimirov *Mekh. Kompoz. Mater.*, 1980(3), 387
13. A I Mel'ker, A I Mikhailin *Fiz. Tverd. Tela*, 1981, **23**(6) 1746
14. A I Mikhailin, A I Mel'ker *Fiz. Tverd. Tela*, 1980, **22**(8) 2518
15. A I Mikhailin, A I Mel'ker *Khim. Fiz.*, 1985, **4**(1) 15
16. M G Zaitsev, I V Razumovskaya, *Vysokomol. Soedin.*, 1979, **21B**(6) 461
17. J H Batech, J D Powell *Solitons in Action* (Edited by K Longren, E Scott) (Translated into Russian), Izd. Mir, Moscow, 1981, p. 269

18. F E Walker, A M Karo, J R Hardy *Non-equilibrium Cooperative Phenomena in Physics and Related Fields* (Edited by M G Velarde), Elsinor, Madrid, 1983, p. 363
19. V S Zhukov *Pis'ma v Zh. Eksp. Teor. Fiz.*, 1983, **38**(11) 523
20. M A Collins *Adv. Chem. Phys.*, 1983, **53** 225
21. T J Rolfe, S A Rice, J Dancz *J. Chem. Phys.*, 1979, **70**(1) 26
22. G A Grigoryan, L S Zarkhin, L I Manevich *Doklady VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel* (Reports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Valgus, Tallin, 1986, Part II, p. 63
23. G A Grigoryan, L S Zarkhin, L I Manevich *Dokladdy VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel* (Rreports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Valgus, Tallin, 1986, Part II, p. 69
24. V A Lagunov *Fiz. Tverd. Tela*, 1985, **27**(7) 2175
25. M Toda *Phys. Lett.*, 1975, **18**C(1) 1
26. L S Zarkhin, S V Sheberstov, N V Panfilovich, L I Manevich *Tezisy Dokladov X Yubileinogo Vsesoyuznogo Simposiuma po Mekhanoemissi i Mekhanokhimii Tverdykh Tel* (Abstracts of Reports of the Xth Jubilee All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Izd. Moskov. Lesotekh. Inst., Moscow, 1986, p. 88
27. L S Zarin, L I Manevich, N S Enikolopian *Makromol. Chem.* (in press)
28. J Forsyth, M Malcolm, K Mowler *Machine Methods for Mathematical Computations* (Russian Translation from English edited by Kh D Ikramov), Izd. Mir, Moscow, 1980, p. 280
29. L S Zarkhin, K Ya Burshtein *Vysokomol. Soedin.*, 1982, **24**B(9) 695
30. L S Zarkhin, K Ya Burshtein, N S Enikolopian *Dokl. Akad.'. Nauk SSSR*, 1987, **293**(1) 133