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Mechanochemical Synthesis

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The mechanism and conditions in the mechanodegradation of certain homochain and heterochain polymers as well as mechanochemical graft and block copolymerisation, polycondensation, and mechanochemical complex formation processes are examined. These yield a virtually complete description of the behaviour of test polymers in mechanochemical processes; the possibility of altering the structure and properties of the initial polymers in the required direction is also discussed. Attention has been concentrated on homopolymerisation and copolymerisation reactions; it is shown that the reaction mechanisms and the structures of the polymers formed possess features determined by the nature of the activating influence (mechanical energy).
The bibliography includes 129 references.

CONTENTS

I. Activation of solids, including polymers, by mechanical energy 283
II. Reactions initiated by active fragments obtained by the mechanodegradation of polymers 289
III. Reactions initiated on inorganic mechanoactivated surfaces 293

I. ACTIVATION OF SOLIDS, INCLUDING POLYMERS, BY MECHANICAL ENERGY

1. Essential Features of the Process

Mechanochemistry is a science developing at the boundary between chemistry and mechanics: it is closely related also to other branches of science and engineering—physics, especially solid state physics, biophysics, physical chemistry, polymer technology, the chemistry and technology of inorganic substances, biochemistry, molecular biology, and bionics.

By selecting and reworking certain facts and laws taken from all these branches of science, mechanochemistry has in its turn put forward its own laws and conclusions, promoting the development and enrichment of the sciences related to it.

In the most general definition, mechanochemistry can be referred to as the science which deals with the study of the interconversions of mechanical and chemical energy in material bodies.[1-3] However, the creation of a single all-embracing hypothesis reflecting comprehensively all the aspects of the mechanochemical process must be based on the knowledge of the complex structure of the test object, which is determined by a number of levels of supermolecular organisation. The mechanochemical phenomenon includes two main components: the mechanochemical component, which determines the conversion of mechanical energy into chemical energy, and the chemomechanical component, which represents the liberation of mechanical energy as a consequence of chemical reactions.

Here one must bear in mind that it is extremely difficult to tell whether the mechanical action is the primary factor inducing the chemical reaction or whether it is merely an agent facilitating the action by the medium. The field of mechanical forces influences the probability of the initiation of various reactions and the latter in their turn determine the spatial disposition of the structural elements[4] (Fig.1).

The chemomechanical aspect of the phenomenon has been discovered as a result of studies by Kuhn[5] and Katchalsky[6] using artificial systems. Similar studies have been carried out also by other investigators.[8,9] These studies are of interest not only because of their current practical value but also because they model important biological phenomena such as the transport of matter through membranes or the contraction of muscle tissue, whose mechanisms have now been virtually demonstrated.[10-23] Different variants of the "mechanochemical machine" have been published, in which the LiBr and NaCl electrolyte concentration gradients and the pH values excite the expansion and contraction of protein (collagen) or cellulose fibres, which are thus able to set in mechanical motion a system of wheels in accordance with the transmission belt principle.[7]

The most complex process responsible for the liberation of mechanical energy in living organisms is the biomechanical process, which is cyclic in character. In muscle contractions, it takes place at the level of supermolecularly organised protein macromolecules, constituting macroscopic systems, which are excited mechanically by the work of the preceeding cycle. In this state, they become the site where chemical reactions (especially of the enzyme type) take place with the biological medium. Thus an isobaric and isometric mechanochemical transformation occurs (Fig.2). Its direct result is a change in the relative disposition of atoms and groups of atoms and also a change in the conformation of the macromolecules. The conformational changes occurring at the level of each macromolecule are manifested in contraction and expansion effects at the level of the supermolecular formation incorporating these macromolecules; as a result, this formation begins to perform mechanical work. The chemomechanical transformation in the cycle (2) is thus performed (Fig.2). The mechanical energy liberated acts on the supermolecularly organised macromolecules and the latter pass to a mechanically excited state and the biomechanical cycle is repeated.[23]

Consequently the mechanochemical process combines both the transformation of chemical energy into mechanical energy and of mechanical energy into chemical energy; the site where these transformations take place is the structure subjected to the given action. The mechanochemical and biochemical processes are now known and many aspects have been investigated; these processes have found important applications in life and engineering[1,2,23-28] (Fig.3).

2. The Step-wise and Activated Character of the Mechanical Process

The step-wise character of the mechanochemical process is manifested when it is considered at different levels of the supermolecular organisation. It is determined by the structural features of the polymer, which determine the specific character of the concentration of mechanical energy in specific chemical bonds located in the zone of defects with a statistical distribution at molecular, supermolecular-morphological, and structural-composition levels.

The micromechanics of the dissociation of chemical bonds can be studied successfully using the oriented polymer model of the greatest mechanical resistance to rupture (having the profile of fibre) or on a single crystal obtained by solid-phase polymerisation.[29] Such structures possess discrete formations, clearly separated in space, with a supermolecular organisation, whose transformation induced by the mechanical action can be estimated with the aid of the usual research methods. The mechanical model of such a structure can be represented as a set of macromolecules maintained in the longitudinal direction by dispersion forces, whose nature depends on the actual chemical structure of the polymer investigated (Fig. 4*a*).

For a correct separation of the phenomena occurring in the volume element under the influence of mechanical energy, account must be taken of the following factors. Real polymers (and material bodies in general) are characterised by a structural inhomogeneity, as a result of which the distribution of mechanical stresses is non-uniform. Since the determination of the magnitude of the stresses in chemical bonds is extremely difficult, one usually determines the variation of the rate constant for the dissociation of overstressed chemical bonds. It is then necessary to know the nature of the factors influencing the probability of the onset of chain mechanodegradation and the nature of the radical reactions initiated in this way.

Simplifying conditions, consisting, for example, of assuming that the stresses are distributed uniformly over each structural and chemical bond element, are usually resorted to in the calculations. For an analytical investigation of the phenomena occurring in a volume element (Fig. 4*a*), an isolated macromolecule, having the flat zigzag shape (Fig. 4*b*) characteristic of the majority of known polymers, is considered. As a result of the action of the stretching force P_1 on this macromolecule, the valence angles and chemical bonds are deformed. According to the condition adopted, the force is distributed in equal parts P_i which act on the

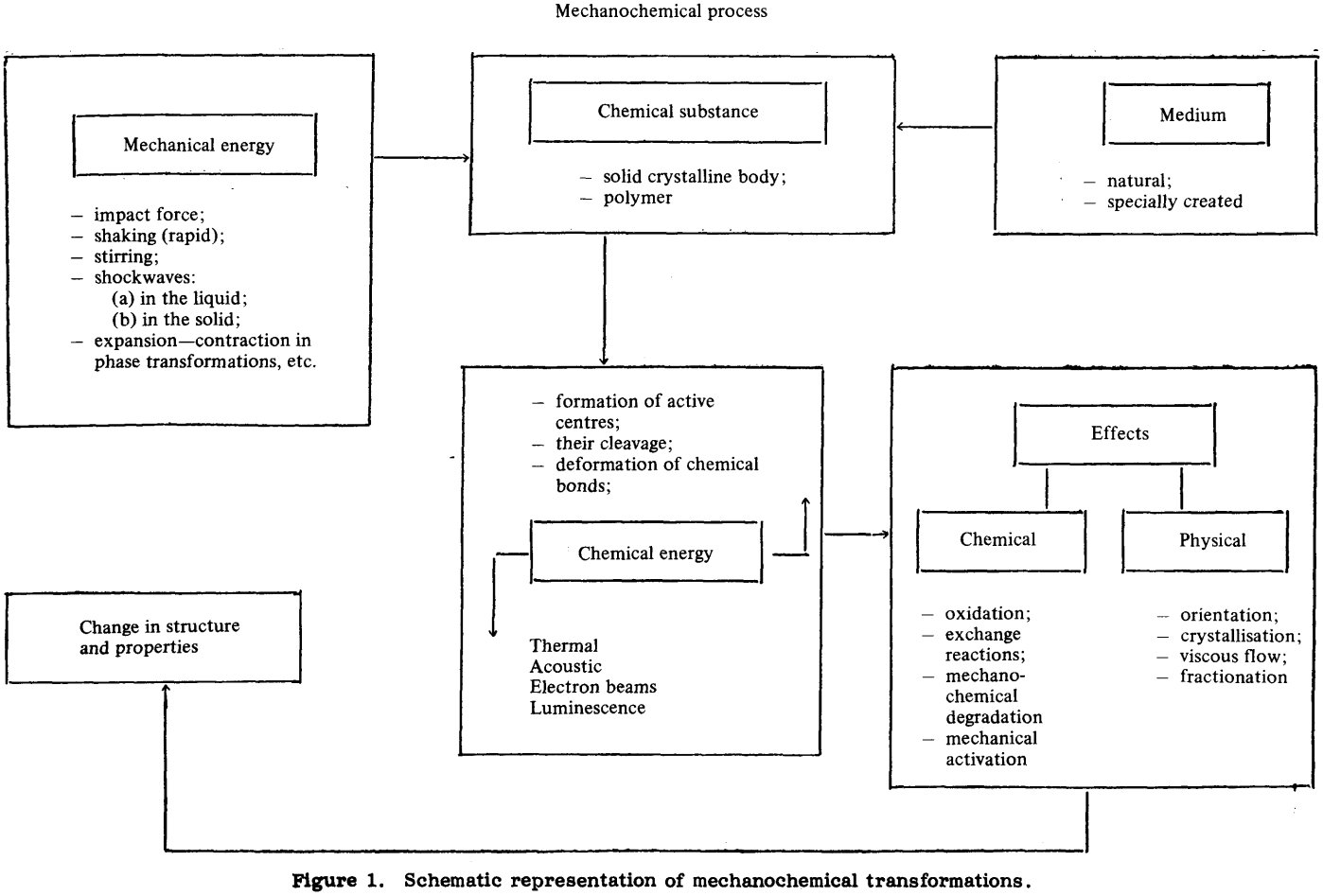


Figure 1. Schematic representation of mechanochemical transformations.

corresponding structural microelements consisting of not less than two chemical bonds (*1–2* and *2–3*) and a valence angle (*1–2–3*) (Fig. 4c) and can be divided into tangential ($P_{i,t}$) and normal ($P_{i,n}$) components. Despite the fact that the deformation of the valence angle is greater, the rupture takes place in the chemical bond. According to Natarajan and Reed,[39] we have

$$P_{t,\max} = \frac{P_{i,t,\max}}{\sin \rho_0} ,$$

where $P_{i,\max}$ is the force causing the dissociation of the chemical bond, $P_{i,t,\max}$ the tangential component at the instant of rupture balancing the resistance of the chemical bond, and ρ_0 the valence angle at the instant of rupture.

The break in the section *BC* (Fig. 4a) occurs when the latter is acted upon by a force which is determined by the length of the macromolecule with the maximum molecular weight ($P_{i,t,\max} = \Sigma n P_{i,t}$). Consequently, the chain length, expressed in terms of the number of component chemical bonds, is important for the occurrence of the rupture process. When the volume element contains macromolecules of critical length (which is much greater than the average length), its stability no longer depends on the energy of the interchain bonds but does depend on the chain length. For the critical chain lengths, the force developed is a maximum and causes the breaking of the chain, i.e. mechanocracking.

The breaking of the chains via mechanocracking is a chemical reaction but of a kind such that the participating kinetic and structural elements are not individual macromolecules but volume elements involved in the rupture. Therefore, despite the fact that the rupture occurs as a result of changes in the bonds at the atomic-molecular level, the mechanical process belongs, in essence, to the supermolecular level.

If the mass of the rupture volume element is denoted by X_2, then, after the absorption of a definite amount of mechanical energy Ω, the volume element is separated into two parts (X):[30]

$$X_2 + \Omega \rightarrow 2X .$$

The absorption of elastic energy leads to a bond dissociation volume element which is non-uniform in different regions. In those microvolumes where the potential energy becomes sufficient to overcome the energy barrier to the transition to the new state, an elementary breaking step, consisting in the transformation of the initial configuration state into another (final) state, takes place. At an intermediate stage, a configuration critical for the given conditions (corresponding to the maximum area under the potential energy curve) is attained, representing an unstable mechanoexcited complex. This complex is stabilised by the excess energy obtained by dissociation of a certain additional number of chemical bonds. The energy accumulated is then distributed among the vibrational and rotational degrees of freedom in accordance with

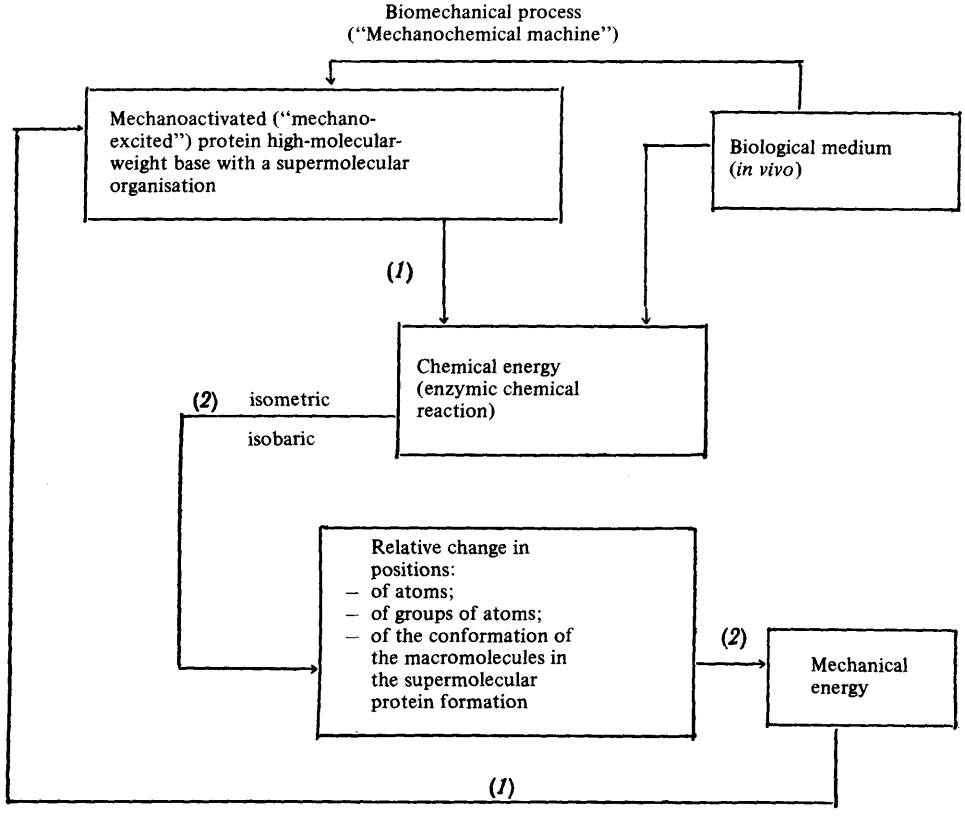
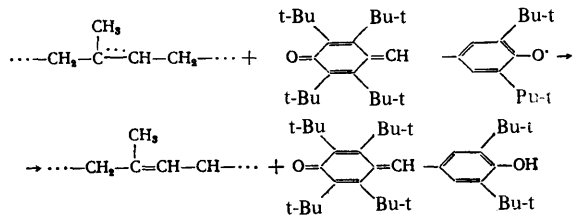


Figure 2. Schematic representation of a biomechanical process: 1) mechanochemical transformation; 2) chemomechanical transformation.

the requirements of the new configurations. Hence it follows that, in the bond deformation stage before rupture, the reactivity of the system increases with formation of mechano-excited states and free radicals, which arise as a consequence of the mechanocracking of the chemical bonds, occurring to a limited extent in the interior of the most activated micro-regions. The set of macroradicals, formed by a certain number of molecular breaks in the mechanoexcited micro-volume, leads to the appearance of an incipient microcrack.

The appearance of a mechanoexcited state and the formation of free radicals have been demonstrated by EPR studies and have been confirmed by the character of certain chemical reactions. For example, raw rubber deformed by stretching is oxidised more readily;[31–33] vulcanised rubber is ruptured more readily on exposure to ozone;[34] certain heterochain polymers are hydrolysed in the cold under the conditions of mechanical action, whilst under the usual conditions this process can occur only at elevated temperatures.[35,36] The mechanoexcited state in raw rubber enables the latter to react with stable radicals of the galvinoxyl type[37] in accordance with the scheme



When certain polyoxoamides are stretched in an inert medium in the cold, free radicals are obtained whose formation may be followed visually since they are coloured red. After the removal of the force, the active centres vanish and so does the colour, but the test specimens become insoluble in *m*-cresol.[38] The stretching of vulcanised rubber without additives at low temperatures (93–193 K) takes place with the appearance, before the onset of rupture, of fine gas

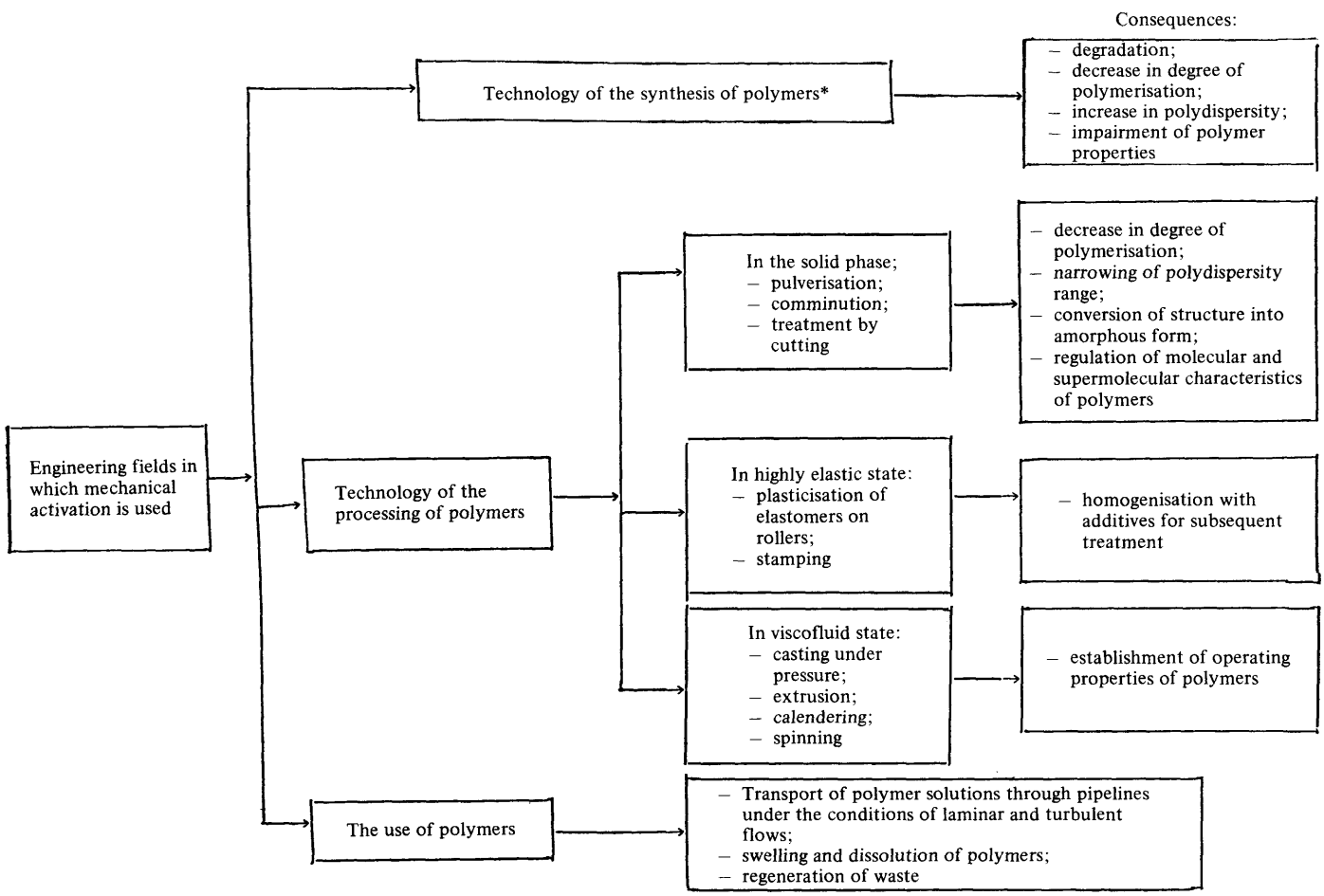


Figure 3. Technical applications of mechanochemical processes.

*Limited under the conditions of vigorous stirring of very viscous media.

bubbles on the surface of the specimens (the "foaming effect"), the gas being shown by chromatographic analysis to be hydrogen evolved on mechanical rupture of the chains. The stretching of the specimens at 93 K with the simultaneous recording of EPR spectra indicates the formation of free radicals. The amount of hydrogen evolved and the concentration of the radicals are correlated with the degree of structure formation in the elastomer and with the applied force (Fig.5 and Table 1).

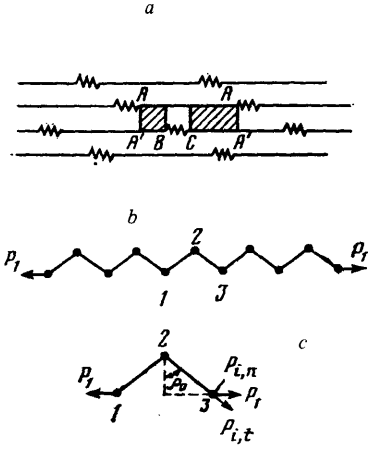


Figure 4. *a*) Mechanical model of a partly oriented polymer;[39] *b*) macromolecules subjected to the action of a force P_1; *c*) microelement subjected to the action of a force P_i.

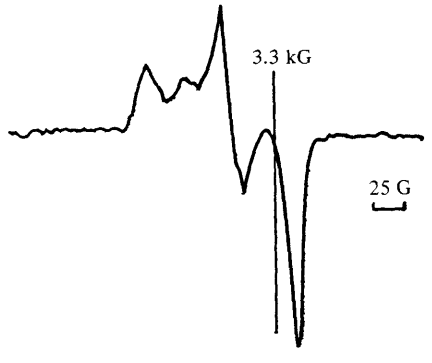
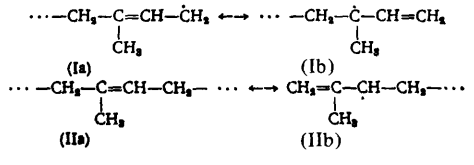
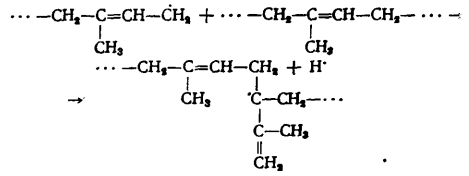


Figure 5. EPR spectrum, recorded at 200 K, of polyisoprene rubber stretched at 366 K.[39]

The results obtained show that the mechanical rupture of the chains takes place with participation of radicals in accordance with the scheme



and confirms the following mechanism:



The increase in the reactivity of the system at the deformation stage before rupture can be accounted for by the appearance of mechanoexcited states and free radicals and is defined by the term "mechanoactivation".

Table 1. Characteristics of polyisoprene rubber specimens stretched at 93 K.[39]

S, %	M_c	M_c^*	$10^{-17}a$, spins g^{-1}	l, cm^3 g^{-1}
1	11 158	10 668	4.0	28
2.5	6 082	5 370	8.9	47
4	4 385	3 850	9.5	50
6	3 364	2 934	11.1	60

Notation: M_C is the initial number-average molecular weight, M_C^* the molecular weight after the evolution of hydrogen, a the concentration of spins before rupture, l the amount of hydrogen evolved, and S the relative elongation of the specimen.

The accumulation of an increasing number of rupture volume elements generates a state promoting degradation; the free energy of the system then increases. For sufficiently high chemical potentials, the mechanochemical phenomena acquire quantitative characteristics to which corresponds the acceleration of all the chemical reactions possible in the given system by factors of tens.[40] The second step in the mechanochemical process, namely mechanocracking, takes place mainly via a radical chain mechanism at the atomic-molecular level. It results in the accumulation of degradation products with the minimum molecular weight (which is determined by the nature of the polymer and the medium, the parameters of the mechanical regime, and temperature), called the degradation limit ($\bar{M}_\infty$). The set of mechanocracking acts inducing the loss of functional properties by the polymer determines the mechanodegradation process.

The third step in the mechanochemical process proceeds mainly at the supermolecular level and consists in the reorganisation of the entire structure of the chain mechanism. This step consists of the following phases: (1) initiation occurring simultaneously with formation of incipient microcracks; this process begins already in the mechanoactivation stage (*A*, *B*, and *C* in Fig.6); (2) the growth of microcracks with formation of macrocracks from the latter (*E*); (3) the conversion of the macrocracks into the main crack capable, by virtue of its size, of generating, at its apex, stresses sufficient for the rupture of the structural element with formation of a new surface (*F* in Fig.6). At the macroscopic level, the specimen is ruptured. The rate of growth of the main cracks in the polymer v is expressed by the equation[41-44]

$$v = C \cdot \exp\frac{U_0 - \alpha\sigma}{RT},$$

where $c \cong 10^{10}$ cm s^{-1} is a constant, U_0 the activation energy for the growth of the main crack, α a coefficient taking into account the stresses appearing at the apex of the crack, σ the external load, R the gas constant, and T the temperature (K) at which the process takes place. The quantity U_0 is numerically equal to the activation energy for the dissociation of chemical bonds. At the instant of rupture, numerous active centres of the radical type appear as a result of the homolytic dissociation of macromolecular chains in the path of the main crack. After their stabilisation, new functional end groups are obtained, as is indicated by IR spectroscopic data.[45] The determination of the number of end groups on the surface of the main crack yielded 0.5×10^{22} cm^{-3}, which is approximately equal to the total number of chemical bonds in one cubic centimeter; consequently the surface of the main crack contains virtually only the ends of the chains.[48]

Both the incipient microcracks, which are active dynamic nuclei, and the main cracks are formed via the same mechanism, which consists in essence in the thermofluctuation rupture of chemical bonds activated by the stresses induced by the mechanical force applied from the outside.[41–47] The formation, growth, and spreading of the cracks via the mechanism indicated above are influenced signficantly by the presence of chemical agents penetrating into the depth of these cracks and accelerating the phenomena activated by the action of the force.

Consequently under the conditions of the stripping and fragmentation of the supermolecular and morphological formations in a solid polymer, the mechanical energy is consumed on the dissociation of interatomic bonds with formation of free radicals and also on the dissociation of ionic bonds (with the appearance of an electrical double layer), which can lead to the formation of new functional groups. Continuously renewed highly activated surfaces, constituting the basis for the initiation of numerous chemical reactions, are thus produced. The chemical reactions can be initiated either in the radical stage of the formation and growth of the cracks or later. The occurrence of these reactions is facilitated by the appearance of new functional groups and by the loosening of the structure of the specimen, which increases the accessibility of the active centres to chemical agents.

3. The Nature of the Primary Active Centres

Analysis of the elementary act in a mechanochemical process should have as its starting point the determination of the nature of the primary active centre appearing on decomposition of the mechanoexcited state.

The molecular transitions from the ground state to the activated state take place from a bonding orbital (π or σ electron) or from a non-bonding orbital (p electron) to an antibonding orbital (π^* or σ^* electron), which disturbs the distribution of the bulk of electron density. This tends to destabilise the chemical bond in the polymer.[47] The energy corresponding to excited states greatly exceeds the strength of any >C–C< chemical bond (Table 2), so that the recombination of the macroradicals generates insufficient energy to excite the neighbouring species (macromolecules, radicals).

Table 2. Electronic transitions for certain polymers (specimens in the form of films).

Polymer	λ_{max}, nm	$h\nu_{max}$, kJ mol^{-1}	Transition
Polyethylene	150	802	$\sigma \rightarrow \sigma^*$
Polybutadiene	180	670	$\pi \rightarrow \pi^*$
Polystyrene	187—200	461—645	$\pi \rightarrow \pi^*$ [a]
Poly(methyl methacrylate)	214	561	$p \rightarrow \pi^*$
Poly(ethylene terephthalate)	290	415	$p \rightarrow \pi^*$
Poly(ethylene terephthalate)	240	502	$p \rightarrow \pi^*$ [a]

[a] Taking into account the π-electron system.

For the idealised case of the dissociation *in vacuo* of chemical bonds of different types ranging from homopolar to purely ionic, two variants of such dissociation can be put forward:

$$\cdots -R_1-R_2-\cdots \longrightarrow \begin{cases} \cdots -\dot{R}_1 + \dot{R}_2 - \cdots \\ \cdots -\overset{(+)}{R}_1 + \overset{(-)}{R}_2 - \cdots \end{cases}$$

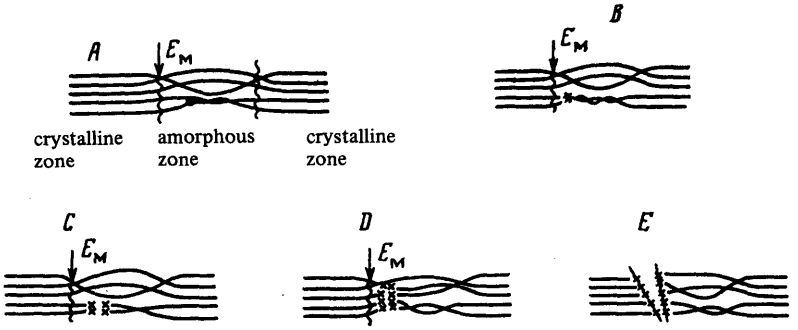


Figure 6. Stages of the mechanochemical process in the degradation of polymers (the arrow indicates the site where the mechanical energy E_m is concentrated—the junction of the crystalline and amorphous zones; the filled circle denotes a structural defect in the amorphous zone; the star denotes a structural defect mechanoactivated by the stress due to the action of mechanical energy E_m).

Positive ions or radical-ion centres with an energy level below that of the excited state appear with the greatest probability. Since the dissociation of ...$-R_1-R_2-$... into molecular ions requires an additional energy equal to 672 kJ mol^{-1} or even more, the above dissociation is more economical from the energetic standpoint than the homolytic dissociation.

After the formation of free radicals, the carbon–carbon bonds located in the α-position relative to the carbon atom with the unpaired electron proved to be to some extent stronger than in the ground state, while the bonds in the β-position are weaker. The subsequent rupture of the hydrocarbon chain containing the radical involves the formation of a double bond and the liberation of energy (250–280 kJ mol^{-1}). This shows that the activation energy is smaller for reactions of this type (Table 3).[47]

Table 3. The activation energies E_a for the rupture of chains containing a radical.[47]

Polymer	E_a, kJ mol^{-1}	Polymer	E_a, kJ mol^{-1}
Polyethylene	118	Poly(vinyl fluoride)	116
Polypropylene	102	Poly(vinylidene fluoride)	131
Polyisobutylene	76	Polytetrafluoroethylene	147
Polystyrene	85	Poly(vinyl acetate)	118
Poly(α-methylstyrene)	95	Poly(methylmethacrylate)	98
Poly(vinyl fluoride)	87	Poly(methyl acrylate)	85
		Polycaprolactam	117

The activation energies for the dissociation of bonds at the atom with the unpaired electron have been calculated by Kagya et al.[48] Free radicals are obtained as a result of the dissociation of chemical bonds not only in organic but also in organoelemental or inorganic polymers. The mechanical dispersion of quartz leads to the liberation of active species,[49–51] whose paramagnetic character has been demonstrated chemically or with the aid of paramagnetic nuclear resonance.[52–54] On mechanical dispersion of $SO_2/BaSO_4$, electrons in the form of *F* or *Y* centres were discovered not only at low temperatures.[2,27] An electrical double layer is formed via the dissociation of adhesion bonds on newly formed surfaces in contact, which generates a very intense electric field. The electrons leaving their initial positions move away from the newly formed surfaces into the bulk of the body, which leads to its electroexcitation. The electrical discharges induced by the activation of solid surfaces in contact and also of the newly formed surfaces liberate electrons which are capable of participating in subsequent mechanochemical reactions.[27]

II. REACTIONS INITIATED BY ACTIVE FRAGMENTS OBTAINED BY THE MECHANODEGRADATION OF POLYMERS

Studies on graft block copolymerisation have been undertaken because of the need to devise processes permitting the synthesis of compounds with the necessary predetermined properties. The aim of such research has been to obtain copolymers whose components would arise from significantly different polymers (natural and synthetic, polar, highly elastic, and rigid), so that the resulting compounds should combine the properties of the initial components.[55–59]

The mechanical activation of graft block copolymerisation is thought to be one of the most economically efficient ways of obtaining new products using the equipment generally adopted for the treatment of the initial polymers. Mechanical grafting was used initially to elucidate the character of the mechanism of the mechanochemical degradation of polymers[1,2,60–64] and only later as a method for the specific transformation of their structures and properties for practical purposes.[65–73]

1. Mechanical Grafting in a Polymer–Monomer System

The initiation of chemical reactions in a polymer–monomer system is due to the presence of radicals formed on cleavage of the polymer macromolecules subjected to mechanical treatment. In principle, the active primary centres should induce the formation of block copolymers in the presence of monomers. However, in practice, the simultaneous occurrence of graft polymerisation is observed, since chain transfer and in certain cases also cross-linking are unavoidable under the conditions of a radical mechanism. At the present time there are no methods which would make it possible to establish their specific contribution to the formation of the final product.

Table 4 presents only a few examples of the numerous systems investigated, which have a bearing on the specific alteration of certain properties of the polymer base. For example, non-polar polymers alter the character of the structure formation processes after grafting with the aid of acrylic acid, maleic anhydride, or a mixture of the above compounds to styrene, vinyl acetate, acrylonitrile, or methyl methacrylate.[68–72]

The improvement of surface-active properties has been achieved by grafting polar monomers to certain polymers of the polyamide[65] or polyester[66,67] type, which made it possible to overcome one of the main disadvantages of synthetic fibres—the lack of exchange of moisture with the external medium. Norbornene and SO_2 polymerise rapidly in the presence of mechanoradicals† formed, for example, from polyisobutene subjected to rapid stirring in solution. This reaction has been recommended as a method for the recognition of free radicals.[72]

2. Mechanochemical Grafting–Block Copolymerisation in a Polymer–Polymer System

A mixture of polymers has been most frequently jointly subjected to a treatment in order to improve technological and operating properties. In many cases the process conditions were the same as those usually employed in technological treatment and in some cases industrial equipment has been used.

In principle, the synthesis is initiated by the usual active fragments obtained by the rupture of macromolecules acted upon simultaneously by mechanical and thermal factors. The reactions of the active centres formed are as a rule subsequently complicated owing to mechano- and thermo-oxidative effects, which are unavoidable when the reaction takes place in the presence of atmospheric oxygen. By acting as a universal radical acceptor, atmospheric oxygen usually accelerates energetically initiated processes.

† Here and henceforth in the review the term mechanoradicals will be applied to radicals formed on mechanoexcitation.

Table 4. Graft block copolymers synthesised in a polymer–monomer system.

Polymer base	Type of active centre		Monomer	Conditions of treatment	Mechano-chemical reaction	Result	Refs.
	1	2					
Poly(ε-caprolactam	NH–CO–$\dot{C}H_2$ *	...–NH–CO–$\dot{C}$H–	Styrene	Vibromilling inert medium; $T = 18 \pm 2$ °C	Graft block copolymerisation	—	[65]
Polyhexamethyleneadipamide	Ditto	Ditto	Vinyl chloride	Ditto	Ditto	—	[65]
Ditto	»	»	Acrylonitrile	»	»	—	[65]
»	»	»	Acrylic acid	Vibromilling, inert medium; T = 196 °C	»	Surfactants	[66]
Poly(ethylene terephthalate)	...–C(=O)–O+ + $\dot{C}H_2$–CH_2–...	...–C(=O)–O–$\dot{C}$H–...	Vinyl chloride, acrylonitrile, vinyl acetate	Vibromilling, inert medium; $T = 18 \pm 2$ °C	»	Hydrophilic properties	[67—81]
Ditto	Ditto	...–C(=O)–OCH_2–$\dot{C}$H–...	Ditto	Ditto	»	Ditto	[67—81]
»	»	Ditto	Acrylic acid	Cryolysis (freezing/thawing cycle); $T = -40$ °C	»	»	[67—81]
»	»	...–C(=O)–O–$\dot{C}$H–...	Ditto	Ditto	»	»	[67—81]
Poly(1,4-*cis*-isoprene), synthetic and natural	...–CH_2–CH=C(–CH_2)–$\dot{C}H_2$	...–$\dot{C}$H–CH=C(–CH_3)–CH_2–	Maleic anhydride	Plasticisation; room temp.	Graft block copolymerisation	Regulates gel formation	[69,70]
Ditto	Ditto	...–CH_2–CH=C(–CH_2OO·)–...	Maleic anhydride jointly with styrene, methacrylate, vinyl acetate, and acrylonitrile	Ditto	Ditto	Ditto	[69,70]
Polyisoprene, natural	...–CH_2–CH=C(–$\dot{C}H_2$)–...	...–CH_2–CH(R)–$\dot{C}$(–CH_2)–... **	Styrene	Plasticisation on rollers	Graft block copolymerisation	—	[71]
Polyisobutylene	CH_3 | ...–CH_2–$\dot{C}$ | CH_3	—	Norbornene + SO_2	Rapid stirring; room temp.	Block copolymerisation	—	[72]
Polytetrafluoroethylene	F | ...–CH_2–$\dot{C}$ | F	CH_2 | ...–CH_2–$\dot{C}$ | C=O | OCH_3	Methylmethacrylate	Vibromilling, inert medium; T = 77 K	Grafting	Hydrophilic properties	[73]
Ditto	Ditto	H | ...–$\dot{C}$–CH_2 | $OCOCH_3$	Ditto	Ditto	Block copolymerisation	Ditto	[73]
»	»	Ditto	Ethylene	»	Ditto	»	[73]

*The radicals were determined by EPR.

**$R^{\cdot} = -CH_2-\dot{C}(CH_3)=CH_2$.

Table 5 presents a series of examples of the synthesis and properties of such products. The treatment of polyethylene (PE) and polypropylene (PP) was carried out both in the presence of certain polar rigid-chain polymers, such as, for example, ethylcelluloses (EC) or ε-polycaprolactam (PC),[74–75,80,81] and certain elastomers.[77–79] The PE/EC system was subjected to a thermomechanical action by plasticisation on a Bradenberg plastograph. It was then shown that the decisive factors in the formation of active centres are the component ratios, process time, and temperatures, while the occurrence of the process itself is influenced significantly by the presence of oxygen, which accelerates the primary radical reactions and leads to cross-linking (Fig.7).[74,75] The PE/PC system was treated by vibromilling at low temperatures

Table 5. Graft block copolymers synthesised in a polymer–polymer system.

Polymer base	Modifying agent	Conditions of treatment	Mechanochemical reaction	Result	Refs.
Polyethylene, low density	Ethylcellulose	Plasticisation on Brabender plastograph; $T = 165$ °C; in air	Graft block copolymerisation; structure formation	The polymer base becomes insoluble; calculation of the fluidity coefficient of the melt; improvement of dielectric properties	[74]
Ditto	Poly(ε-caprolactam)	Vibromilling in an inert medium; $T = 0$–-40 °C	Ditto	Increase in hydrophilicity	[75]
Polyethylene, high density	Polyisobutylene	Extrusion; $T = 150$–260 °C	Graft block copolymerisation	Increased breaking strength; increase in elongation	[76]
Ditto	Polybutadiene + metals (Zn, Mg)	Extrusion; $T = 170$–210 °C	Graft block copolymerisation; structure formation	Increase in density; improvement of fluidity; improvement of resistance to thermo-oxidative influences	[77]
»	Butadiene-styrene copolymer	$F_M = 1.5 \times 10^9$ dyn cm^{-2}	Ditto	Increase in breaking strength	[78]
»	Isoprene-styrene copolymer	Ditto	»	Ditto	[78]
»	Epoxide oligomers	Rolling; $T = 130$–140 °C	Graft block copolymerisation; structure formation	Improvement in mechanical strength	[79]
Polypropylene	Poly(ε-caprolactam)	Extrusion; $T = 200$–210 °C	Ditto	—	[80]
Ditto	Methyl acrylate–sodium alkane-sulphonate copolymer	Extrusion; $F_{cut} = 1.5 \times 10^9$ dyn cm^{-3}	»	Improvement in susceptibility to dyeing	[82]
Polypropylene	Styrene-styrenesulphonamide copolymer	Ditto	»	Ditto	[82]
Poly(vinyl chloride)	Butadiene–acrylonitrile copolymer	Extrusion	Graft block copolymerisation	Improvement in impact strength	[88]
Ditto	Ditto	Rolling; $T = 150$–190 °C	Graft block copolymerisation; structure formation	Improvement in breaking and impact strength	[84–86]
»	Polyurethane elastomers	Ditto	Ditto	Ditto	[84–86]
Butadiene–styrene elastomers, butadiene–acrylonitrile copolymer	Thermoreactive resins of the resol type	Plasticisation of Brabender plastograph	»	»	[87]
Raw rubber or rubber soles (waste)	Phenol-formaldehyde resins	Rolling	Graft block copolymerisation	»	[88, 89]

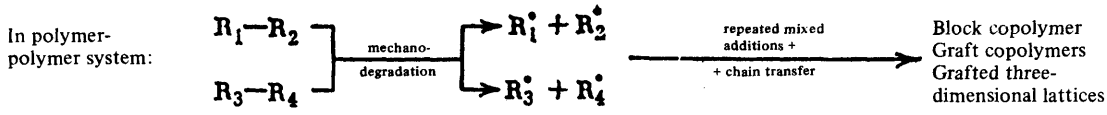
Notation: F_M = mechanical force, F_{cut} = cutting force.

($T = 0$– -40 °C). The rigidity of the system, which is the main condition for treatment in accordance with this principle, was ensured by the presence of a polyamide component and also by the temperatures employed.[76]

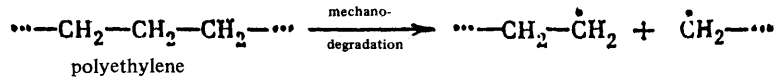
In both cases the main result of the mechanosynthesis is that the polyolefin base becomes insoluble in specific solvents. In the pairs investigated, PE is the component responsible for structure formation, while grafting-block copolymerisation increases the mechanical strength and thermal stability.[78–80] The impact strength and resistance to rupture of poly(vinyl chloride) (PVC) improved appreciably on coextrusion of plasticisation of this polymer on rollers in the presence of elastomers[84–87] (Tables 5 and 6).

The intense influences to which the PVC–elastomer systems are subjected during treatment on rollers favour the occurrence of the grafting–block copolymerisation–structure formation reactions (Table 6). An increase in temperature promotes mainly the occurrence of the structure formation reaction, which ensures an increase in the resistance to rupture, whilst maintenance at low temperatures stimulates mechanochemical grafting–block copolymerisation, which is responsible for an appreciable growth of impact strength. In all the cases investigated, it was possible to establish a 100% increment in the resistance to rupture and impact strength, which is an outstanding result bearing in mind that in the most common cases the factors which improve one of these characteristics impair the other. The solution of equations expressing the dependence of the mechanochemical properties of the reaction products on the thermomechanical conditions made it possible to establish the optimum conditions for the treatment of a PVC–elastomer mixture on rollers.[85–87]

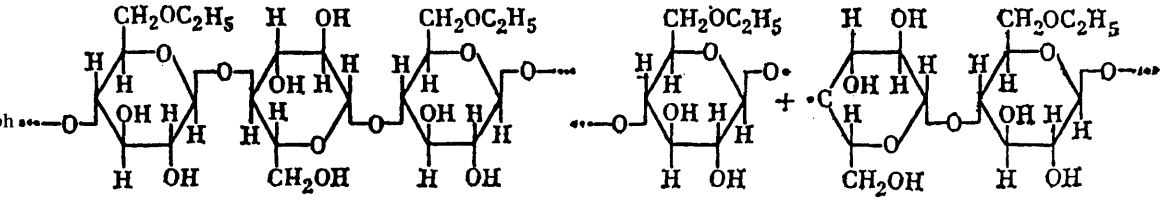
Mechanosynthesis in a polymer–polymer system (in the case of the system comprising waste from rubber articles and thermoreactive resins) leads to the formation of materials with improved physicomechanical properties.[87–89]

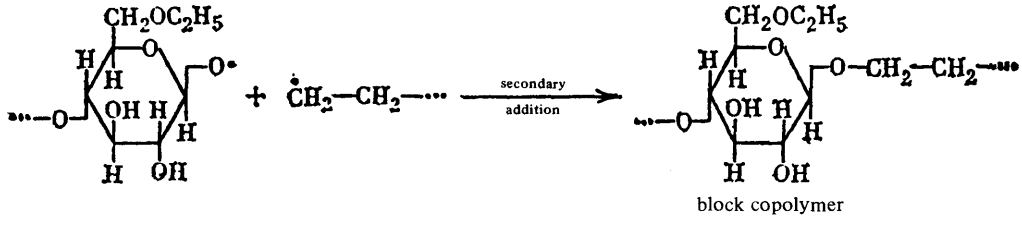


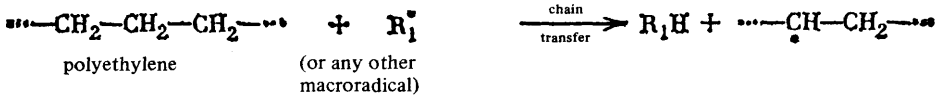
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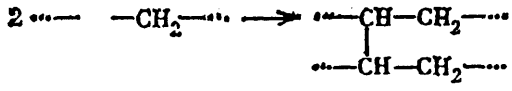


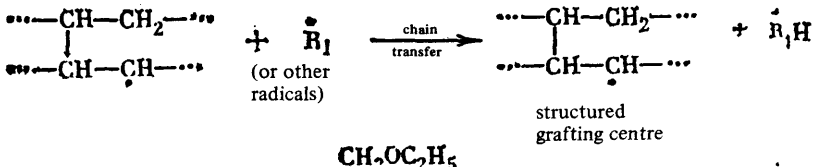
Plasticisation with the aid of Brabender plastograph











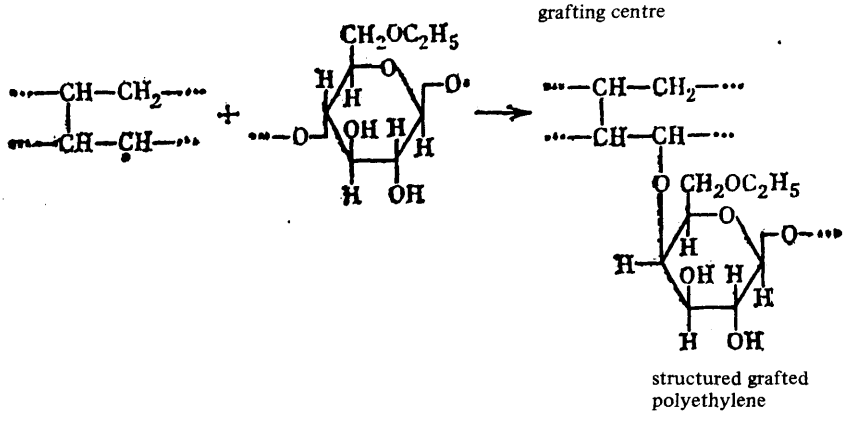


Figure 7. Mechanochemical reactions occurring in the mechanosynthesis in a polymer–polymer system.

III. REACTIONS INITIATED ON INORGANIC MECHANO-ACTIVATED SURFACES

1. Mechanochemical Grafting on Inorganic Surfaces

The mechanochemical activation of inorganic surfaces and the ability of such surfaces to activate chemical reactions have already long been known.[90–106] During the last decade, much attention has been devoted to the study of the mechanisms of these reactions and the elucidation of the nature of the centres inducing them.

Table 6. Variation of certain physicomechanical properties (%) of the PVC–elastomers systems as a function of the conditions of treatment*.[86–87]

Parameters of treatment on rollers*	Value of parameter	Nitrile rubber (SKN-18)		Polyurethane rubber	
		σ_p	a_k	σ_p	a_k
Duration of treatment, min (at $T = 170$ °C)	7	118	138	115	200
Ditto	14	117	258	115	136
"	21	116	233	115	156
Temperature of treatment, °C (for $\tau = 14$ min)	150	120	172	117	148
Ditto	170	117	258	115	136
"	190	115	90	119	216

Notation: σ_p is the resistance to breaking and σ_k the impact strength.
*For the system with 8% SKN and 2.5% PVC

The disintegration of ionic crystals such as those of $CaCO_3$, $BaSO_4$, rock salt, KCl, LiF, and CaF_2 leads to their activation, the degree of which has been estimated from their electron-donating capacity measured by EPR spectroscopy.[107] The surfaces obtained as a result of the grinding of the crystals are characterised by the emission of electrons and by the ability to initiate the grafting of certain vinyl monomers, especially styrene.[107–109]

The correlation between the change in the intensity of the electron emission during the mechanical breakdown *in vacuo* of ionic crystals (NaCl, LiF) and the degree of grafting of polystyrene to the newly formed surfaces indicates a shift in the development of these two effects, namely the grafting continues for a long time after the electron emission has ceased (Fig. 8). Consequently the initiation of the graft polymerisation is induced by the radicals generated on these surfaces by the electronic charges which persist for a long time after the rupture of the crystals.[107] Thus one may speak of an after-effect associated with the reactivity of the electrically charged active centres on the surfaces of the dispersed crystals.

In order to discover the nature of the active centres initiating polymerisation, a study was made of the influence of water vapour on the course of the grafting process. The moisture content of the crystal and the area of its contact surface with the monomer proved to be decisive factors for the process. For each type of crystal, there is a range of moisture contents within which the electrical potential and the degree of grafting reach a maximum. There exists therefore a selective catalytic influence exerted by the amount of water vapour which determines the reactivity of the inorganic surface newly formed as a result of the break up of the crystals.[110] On the other hand, the disintegration of such crystals *in vacuo* (10^{-6} mmHg) in the absence of moisture does not induce grafting. Consequently the adsorption of water vapour on electrical centres favour the formation of the polymerisation initiator. Under the influence of the static electricity on the mechanodispersed crystal surface, the water molecules dissociate and the resulting hydrogen ions ensure the cationic initiation of the polymerisation of styrene. The introduction of hydroquinone into the reaction medium does not disturb the grafting process, which is an additional argument in support of the cationic mechanism.

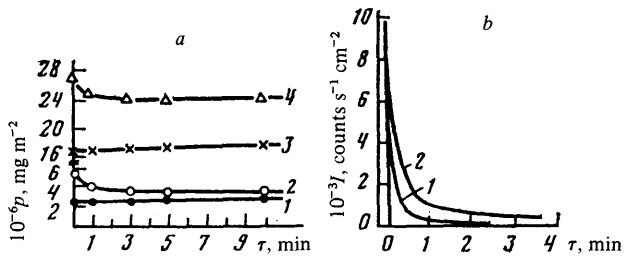


Figure 8. *a*) Dependence of the specific degree of grafting p of polystyrene on time τ after the breaking of the crystal in the liquid monomer and in argon with subsequent immersion in the monomer [1) and 2) NaCl; 3) and 4) LiF]; *b*) time decay of electron emission I from different crystals [1) NaCl; 2) LiF].[107]

Together with the grafting on the surface, homopolymerisation takes place on a limited scale; a radical mechanism has been attributed to such homopolymerisation on the basis of the observed consumption of hydroquinone. Presumably these two reactions—grafting and homopolymerisation—have a common initiation mechanism involving the active centres formed on the inorganic surface. In those cases where the degree of polymerisation of the grafted chains exceeds a certain specific value, the chains undergo homolytic rupture and the mechanoradicals formed combine with hydroquinone. Styrene, which is a nucleophilic monomer, should react with the positively charged centres formed as a result of the dissociation of water vapour. The polymer macromolecules should enter into a physical interaction with the negatively charged centres present on the surfaces formed.

This mechanism has been confirmed by the unipolar character of the charge arising on the surface produced by the breaking of the LiF crystals. When the crystals are broken into two parts, the corresponding rupture surfaces carry charges of opposite sign at the contact points, which results in the formation of a mosaic pattern in the charge distribution on the surface (Fig. 9).

The degree of grafting of styrene relative to the overall area of the negatively charged surface exceeds the degree of grafting relative to the area of the positively charged surface. Furthermore, fluorescence analysis of the products grafted on KCl powders established that the K and Cl contents in the grafted polystyrene are respectively 0.27 and 0.71%; this indicates the breakdown of the stoichiometric composition of the support, which can be explained by the irreversible

interaction of the polystyrene macromolecules with halide ions and the negatively charged centres on the newly formed surfaces of the crystal.

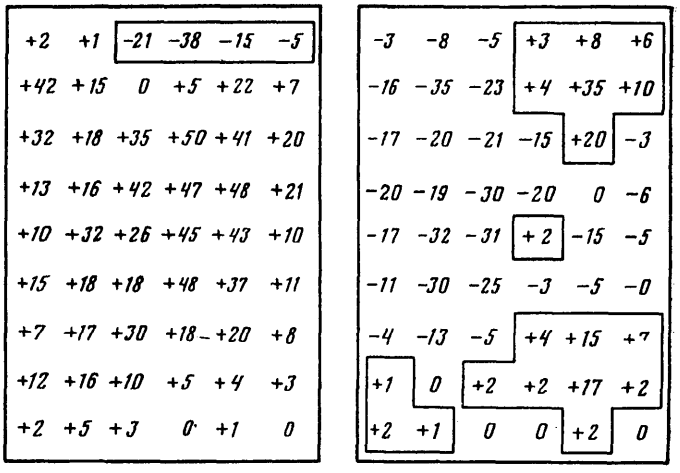


Figure 9. Topography of the distribution of electric charges on the surface of LiF crystals (5 × 10 mm² surface); the numerals indicate the charge intensity in 10^8 e cm^{-2}. [110]

The mechanochemistry of the quartz and sand surfaces is being vigorously investigated, but the existing contradictions have not yet been eliminated from this field. The main problem in the given instance is the elucidation of the nature of the active centres. It has been shown that, firstly, the mechanodispersion of quartz at a residual pressure of 10^{-3} to 500 mmHg in the presence of hydrogen at 80–400 K entails the dissociative chemisorption of hydrogen. [52–54] The active centres combining with hydrogen are formed both as a result of the mutual friction between these particles. The adsorbed hydrogen is firmly attached to the inorganic surface and its removal is possible only on raising the temperature to 600–700 K. On the basis of NMR and IR spectroscopic data, the reaction between quartz and hydrogen can be represented schematically as follows: [101]

$$\equiv Si-O-Si\equiv + H_2 \rightarrow \equiv SiH + SiOH \ .$$

The reaction is caused not only by radicals, which can be detected by EPR, but also by mechanoexcited $\equiv Si-O-$ bonds, since the total number of active centres on the surface is an order of magnitude higher than the surface concentration of free radicals (10^{13} cm^{-2} compared with 10^{12} cm^{-2}).

The primary act in the mechanochemical reaction between quartz and oxygen is the addition of O_2 to the radicals $\equiv \dot{S}i$ obtained on dissociation of the $\equiv Si-O-$ bond: [103]

$$\equiv Si-O-Si\equiv \xrightarrow[E_m]{} \equiv \dot{S}i + \dot{O}Si\equiv Si + O_2 \rightarrow SiOO^{\cdot} \ ,$$

$$\equiv SiOO^{\cdot} + {}^{\cdot}OSi \xrightarrow{\text{recombination}} \equiv SiOOOSi\equiv$$

peroxy-compound .

where E_m is the mechanical energy. The scheme presented above agrees with the consumption of oxygen and the concentration of paramagnetic centres. There is a possibility of the thermal decomposition of the final peroxy-compound:

$$\equiv SiOOOSi \xrightarrow{\Delta} \equiv SiOSi\equiv + O_2 \ .$$

This reaction explains the thermal desorption of oxygen at high temperatures.

Table 7. The adsorption characteristics of certain organic compounds in the vibromilling of sand.

Compound	s, Å²	$10^{-18}N_1$, molecules g^{-1}	$10^{-18}N_{50}$, molecules g^{-1}	N_1+N_{50}, m² g^{-1}
$CH_2=C(CH_3)COOCH_3$	34.3	3.0	4.9	2.7
$(CH_3)_2CHCOOCH_3$	36.1	2.1	1.3	1.2
$CH_2=CHCOOCH_3$	30.8	3.1	4.6	2.4
$C_6H_5COOCH_3$	32.1	2.7	1.2	1.2
$CH_3COOCH=CH_2$	31.2	2.7	1.0	1.2
$CH_3COOC_2H_5$	32.5	2.7	1.0	1.2
$CH_2=CH(CH_2)_4CH_3$	41.4	1.6	0.57	0.91
p-C_7H_{16}	42.5	1.3	0.57	0.80
$(CH_3)_2CO$	28.9	3.3	1.2	1.2
p-$C_2H_5NH_2$	29.0	4.1	2.5	1.9
$(p$-$C_3H_7)_2NH$	40.7	2.8	1.6	1.8

Notation: s is the area of the molecules, N_1 the number of molecules adsorbed per mole of SiO_2, and N_{50} the same number after milling for 50 min.

The mechanical activation of the SiO_2 surfaces can also be accounted for by the grafting of certain vinyl and acrylic monomers in the vapour state (Table 7). [111] Under milling conditions, the monomers gradually polymerise on the solid surface. Oxygen exerts an inhibiting effect on this reaction, while the adsorption of the vapours of organic compounds has no influence on it whatsoever, which indicates a radical character of the process. Although free radicals were not detected under the experimental conditions (by EPR), milled sand contains numerous electrons in the surface traps while the adsorption of organic vapours induces exo-electron emission. [112] Homose et al. [111] therefore proposed a mechanism for the process which begins with electron transfer to the adsorbed monomer, attached to the surface by hydrogen bonds, with the subsequent formation of a radical-ion, which induces in its turn a reaction involving radicals.

2. Mechanochemical Homopolymerisation and Copolymerisation

Evidence confirming the idea that mechanical energy can induce the polymerisation reaction was obtained as a result of studies on polymers in the solid phase. Adler et al. [112] concluded that the elimination of rigorous order from the structure of the crystal lattice influences significantly the the rate of propagation of this type of polymerisation. With the aid of microscopy in polarised light, they demonstrated that polymerisation takes place precisely at the edges of the crystal irregularities. As the polymer is formed, the volume of the lattice diminishes and mechanical stresses appear in it favouring the dissociation of chemical bonds. Under these conditions, new active centres arise in the reaction medium and accelerates the polymerisation, which is initiated in most cases by radiation. Hence it follows that the mechanochemical act plays a significant role in the successful carrying out of the polymerisation process in the solid phase.

Another argument in support of the mechanochemical hypothesis concerning the solid-phase polymerisation is provided by experiment of Bamford et al. [113] involving the

grinding of acrylic and methacrylic acid crystals.[113] These crystals are subjected to a pressure of 1–5 atm directed at right angles to the axis of the crystal lattice. After irradiation with UV light, it was established that the polymerisation takes place without initiators precisely in the regions where the crystals were ground. Thus the idea was put forward that for this type of polymerisation the role of the mechanochemical act is not confined to that of an accelerating factor, because it can also induce initiation. Subsequently, using the energy of a high-intensity shockwave,[114,115] the ability of mechanical energy to induce true polymerisation involving all the stages of the chain mechanism was demonstrated.

Kargin and co-workers[116] used vibration dispersion for the polymerisation of a solid monomer—sodium acrylate. The authors assumed that the process was initiated by the concentration of mechanical energy on structural defects. The energy-induced transition of an electron located in the immediate vicinity of the COO^- group, involving an electron vacancy in one of the lattice sites, leads to the formation of a radical.

Under the experimental conditions used in the above study,[116] acrylamide did not polymerise, so the authors concluded that the ionic nature of the crystal lattice of the monomers plays a significant role.

A number of investigators[117–122] developed a polymerisation method which is activated by "mechanoinitiators"–inorganic crystalline salts with uncompensated electrons, the so-called "electron traps". Under the conditions of vibration dispersion, these electrons migrate to the newly formed surfaces and initiate polymerisation.

Subsequently it was possible to carry out the polymerisation and copolymerisation of a large number of a wide variety of monomers under the conditions of vibromilling without initiating additives. The starting materials (vinyl, acrylic, diene, and cyclic monomers or monomers which cannot be polymerised by the usual methods), were used in the solid (acrylamide, ε-caprolactam, etc.) or liquid state.[123–129]

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