

Structural Changes and Electrodynamic Effects in Polymers under Fast Uniaxial Compression

Aleksey. I. Aleksandrov, Ivan A. Aleksandrov, Vitaliy G. Shevchenko*, and Aleksandr N. Ozerin

N.S. Enikolopov Institute of Synthetic Polymeric Materials RAS 117393 Moscow, Profsoyuznaya, 70 Russian Federation

Abstract Rheological explosion in polymers under uniaxial compression in an open volume occurs at the end of continuous rapid plastic deformation after several stages of creep. Two types of polymers were chosen for this study: brittle glassy amorphous polystyrene and thermoplastic semi-crystalline polypropylene. Electric pulses were detected during explosion, and their spectra were analyzed with two models. X-ray diffraction methods were used to investigate changes in the structure and morphology of polymers during deformation and rheological explosion. The pores appear in polymer in this process, and their shape and size distribution were derived from X-ray experiments. The main reason for the formation of pores in polymer samples in rheological explosion experiments is the intense microshifts in the polymer volume under the action of high applied pressure.

Keywords Polystyrene; Polypropylene; X-ray; Mechanical properties; Compression

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INTRODUCTION

Behavior of various substances under high pressure and shear deformations was first investigated in the thirties of the 20th century, and is still of interest to many researchers.^[1–12] Bridgman was the first to record emissions of matter from the high-pressure zone with open boundaries, which were accompanied by intense sound effects and dispersion of the substance.^[1,2] Bridgman called this phenomenon a mechanical explosion, and later, the name ‘rheological explosion’ was firmly entrenched in it.^[3–12] Interest in this phenomenon is not weakening, since it is directly related to problems of the transition of destructible material from a brittle to a plastic state under dynamic inelastic compression.^[3,4] It is related to resistance of ceramics, glass, and metal alloys to instant destruction.^[5,6] Acoustic and mechanical effects are accompanied by electrical phenomena. Recently, it was found for polymer composites—multiferroics based on a polystyrene (PS) matrix containing binuclear organoelement complexes (QH)₂Co···O···Co(QH)₂ or (QH)₂Mn···O···Mn(QH)₂ (QH is a ligand based on 3,6-di-*tert*-butylpyrocatechol) that during mechanical activation by a rheological explosion, radio-frequency superradiance is observed.^[8–14]

At present, there is no information as to what happens to polymer matrix during a rheological explosion,^[8–12] although it is obvious that the change in its structure and the physico-chemical processes that occur during this explosion have a

significant impact on charge transfer and the formation of a radio frequency pulse.

The aim of this work was a comparative study of the change in the structure of polymer matrices having different plasticity during deformation and rheological explosion. Accordingly, two types of polymers were chosen for this study: brittle glassy amorphous polystyrene and thermoplastic semi-crystalline polypropylene.

EXPERIMENTAL

A special high-pressure cell was used to study the processes during compression and rheological explosion (RE). This cell was placed in the IS-500 compression machine (Fig. 1a). Samples of polymers (10 mm in diameter and 2 mm in thick) were subjected to rapid uniaxial compression at a pressure of ~1–2 GPa and compression rate of 0.5 GPa/s. After explosion the thickness of the films was 300 μm, so X-ray studies were performed using initial and deformed samples of this thickness. The cell (Fig. 1a) is electrically isolated from the press equipment and consists of Bridgman anvils (1 in Fig. 1a), steel cage (2 in Fig. 1a) and punches (5 in Fig. 1a), also electrically isolated from the cage, between which the test sample is located (3 in Fig. 1a). The punches are connected via a 50 Ohm load resistance to Tektronix MSO 200 two-channel digital oscilloscope (6 in Fig. 1a). The cell allows registering alternating current $J(t)$ generated by the electrical component $E(t)$ of electromagnetic radiation emitted in the sample during rheological explosion.

Industrial grade polymers were used to prepare the samples: PSM 115 polystyrene (Salavatnefteorgsintez OAO

* Corresponding author, E-mail: shev@ispm.ru

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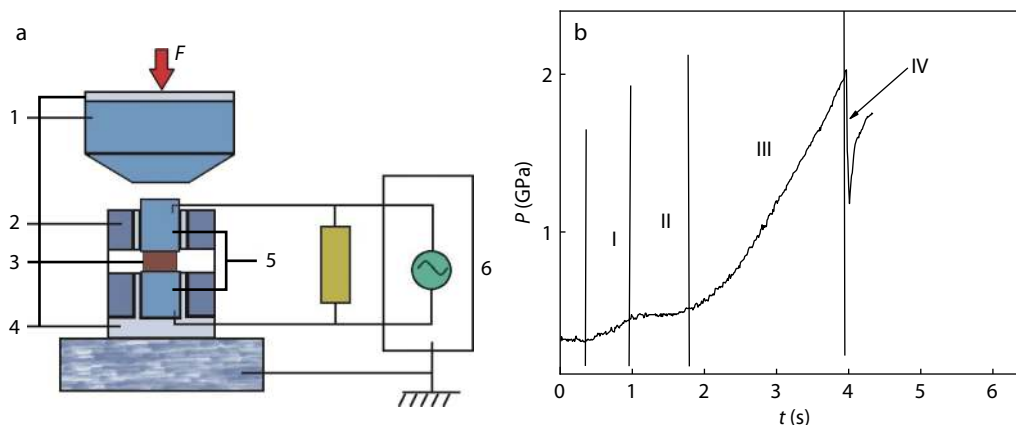


Fig. 1 (a) A diagram of a high-pressure cell: Bridgman anvil (1), steel cage (2), test sample (3), insulation (4), punches (5), digital oscilloscope (6); (b) Time evolution of rheological explosion in polymer sample.

Russia, MFR 5.3 g/10min, $T_g=100$ °C^[15]) and 01030 Kaplen polypropylene (Gazpromneft - Moscow Refinery, MFR 2.9–3.5 g/10min, glass transition temperature $T_g=-10$ °C).^[15] The diffraction patterns show that characteristic reflections of α -phase and β -phase of *i*-PP are present.

The first series was made up of polystyrene (PS) samples: PS0—initial undeformed sample; PS1—polystyrene sample that experienced rapid uniaxial compression up to 1.6 GPa without rheological explosion; PS2—a polystyrene sample that experienced rapid uniaxial compression and a rheological explosion at 2.2 GPa.

The second series included the following polypropylene samples (PP): PP0—the initial undeformed sample; PP1—polypropylene sample that experienced rapid uniaxial compression up to 1.6 GPa without rheological explosion; PP2—polypropylene sample that experienced rapid uniaxial compression and a rheological explosion at 2.0 GPa.

The changes of nanoheterogeneous structure of polymer samples were traced using scanning electron microscopy (SEM), X-ray scattering at large (WAXS) and small angles (SAXS). Since the use of these research methods directly in the process of deformation is impossible for the experimental setup shown in Fig. 1 (SEM) or difficult to implement (WAXS and SAXS), the change in the structure of deformed samples was controlled in post-processes, after the deformation and unloading of the samples were completed. Micrographs of the surfaces of the samples were taken with JEOL-5300LV scanning electron microscope. Electron paramagnetic resonance spectra were recorded using Varian E12a electron spin resonance (ESR) spectrometer at 77 K for samples that were quickly placed in liquid nitrogen (77 K) immediately after the explosion. X-ray diffraction studies at large scattering angles were performed using Bruker D8 Advance diffractometer (CuK α radiation, a focusing Ge monochromator on the primary beam, pass-through mode). The scattering intensity was recorded in the range of scattering angles $2\theta=10^\circ-60^\circ$.

SAXS studies were carried out on a Bruker Nanostar setup (CuK α radiation, three-point collimation scheme, two-dimensional gas detector HI-STAR). The scattering intensity was recorded in the range of the scattering vector modulus $s = 4\pi\sin(\theta)/\lambda = 0.007-0.2$ Å⁻¹ (where 2θ is the scattering angle), which made it possible to analyze scattering from the scatter-

ing phase particles with sizes from 30 Å to 800 Å.

To analyze small-angle scattering, we used the GNOM, DAMMIN, DAMMIF, DAMAVER, and SUPCOMB procedures of the ATSAS 2.4 software package,^[16] based on the use of the Tikhonov regularization method.^[17] The GNOM procedure was used to calculate the scattering curves $I_{\text{reg}}(s)$, optimized over the entire range of scattering angles, the distribution function of the distances in the particle, the integral values of the radii of inertia of the particles of the scattering phase, and the particle size distribution. To determine the shape and spatial structure of scattering particles in the framework of the model of “virtual” (dummy) atoms, the DAMMIN and DAMMIF procedures were applied, based on the application of Monte Carlo method with superimposed simulated annealing. The structures reconstructed in individual runs were averaged using the DAMAVER and SUPCOMB procedures.

RESULTS AND DISCUSSION

Rheological explosion in PS and PP under uniaxial compression in an open volume occurs at the end of continuous rapid plastic deformation after stages of unsteady creep (I in Fig. 1b), steady creep (II in Fig. 1b) and accelerated creep (III in Fig. 1b). These three stages of creep have been studied in detail and reviewed in the literature.^[1–4] Stage III ends with an instant destruction of the polymer, a rheological explosion—this is the fast stage IV in Fig. 1(b); in this case, the material is ejected from under the punches with a strong acoustic effect.

Electrodynamic Effects

Mechanochemical reactions are associated with the formation of an electron-hole pair upon detachment of a hydrogen atom from the polymer chain $H > H^+ + e^-$.^[7] Indeed, ESR method (Fig. 2) showed that during a rheological explosion, $-RO_2^*$ radicals appear in both PS and PP, identified by the appearance of a characteristic ESR spectrum—an asymmetric singlet with $g_\perp=2.005$ and $g_\parallel=2.034$. The appearance of $-RO_2^*$ radicals is usually associated with the addition of oxygen at the site of detachment of hydrogen atom in the polymer chain.^[18] The elastic wave impulse from RE results in acceleration of local molecular mobility of macromolecular fragments and partial ionization of individual atoms or fragments of the polymer

chain. Then, the generation of electric current pulse can be explained on the concept of the appearance of radio frequency radiation during mechanochemical reactions,^[7–9,11] when a radio frequency electromagnetic wave range provides the electron transfer process, *i.e.*, the electric current pulse $J(t)$ - $E(t)$ (Figs. 3a and 3b).

In turn, this electromagnetic wave is associated with charge density fluctuations. The Fourier analysis of current pulses $J(t)$ - $E(t)$ showed that the spectrum of the observed radio frequency radiation lies in the frequency range 0 MHz to 150 MHz. As can be seen from Figs. 3(c) and 3(d), the Fourier

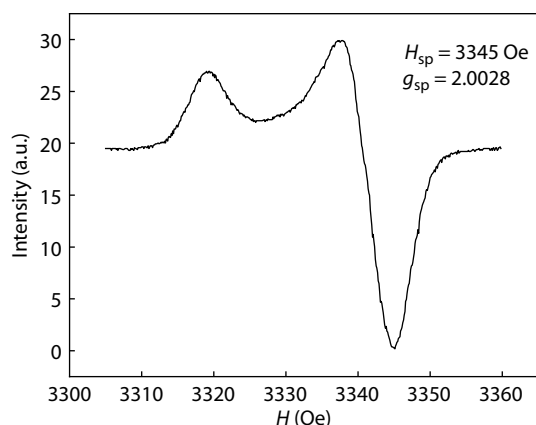


Fig. 2 The EPR spectrum of $-\text{RO}_2^*$ radical.

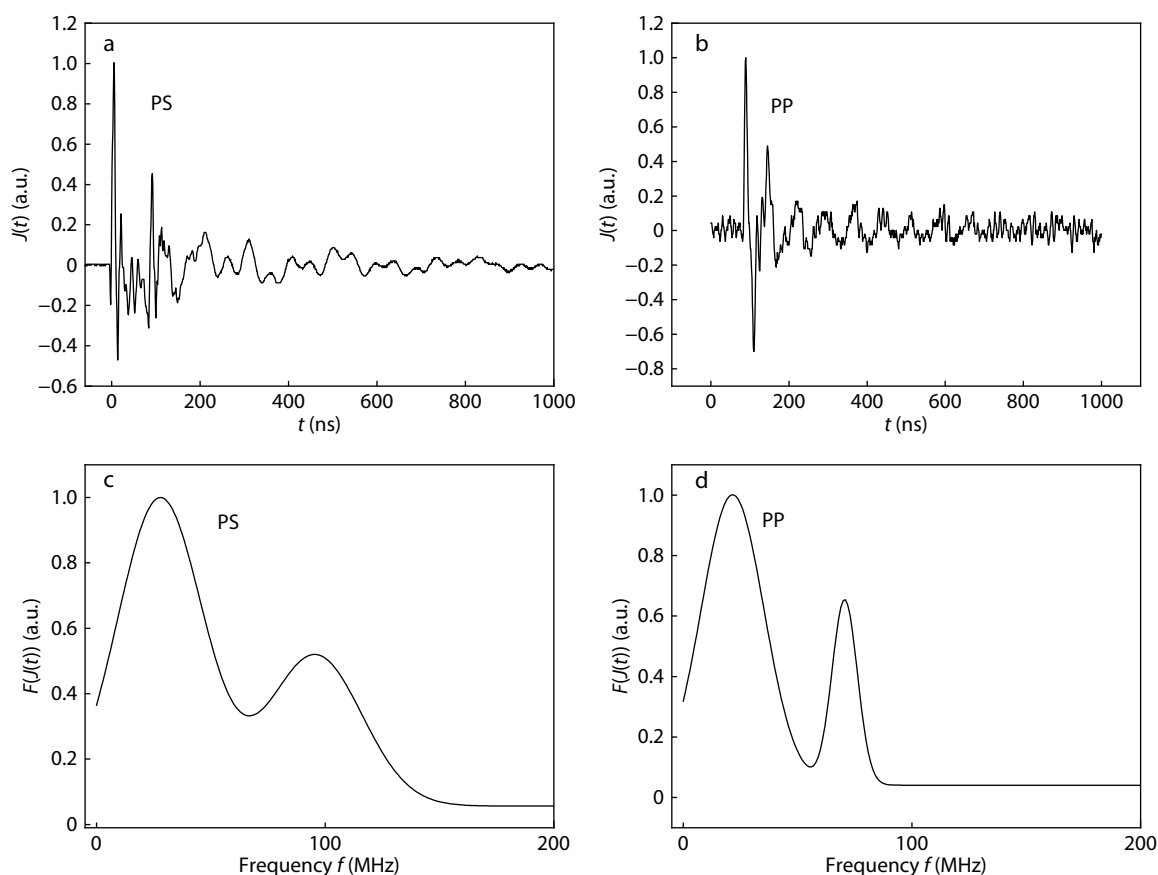


Fig. 3 The current pulses $J(t)$ during the rheological explosion of (a) PS and (b) PP; and their Fourier transforms $F(J(t))$ for (c) PS and (d) PP.

transforms of the signals $F(E(t))$ - $F(J(t))$ have the form of band spectra due to the emission from individual excited molecules that are not or weakly coupled to each other. Radiation is either by electronic transitions in atoms or vibrational movements of the atoms themselves in molecules; therefore, the spectra of such systems can be described in terms of the Lorentz model of harmonic oscillator with damping,^[19] which corresponds to Eqs. (1) and (2):

$$\ddot{\vec{r}} + 2b\dot{\vec{r}} + \omega_0^2\vec{r} = \frac{q}{m}\vec{E} \quad (1)$$

$$E(t) = E_0 e^{-i\omega t} \quad (2)$$

where r is the relative position of the dipole atoms and q is the dipole charge.^[19] Moreover, since r changes with the passage of the elastic wave, polarization vectors $\vec{P}$ respectively change. According to electrodynamics, forced vibrations of charged particles lead to polarization of the medium, which for non-interacting particles of the same type is described by a polarization vector $\vec{P}$, equal to $n\vec{p}$ where n is the concentration of particles, and $\vec{p} = q\vec{r}$ is the dipole moment of the particle. Then Eq. (1) can be rewritten in the form:

$$\ddot{\vec{p}} + \gamma\dot{\vec{p}} + \omega_0^2\vec{p} = \epsilon_0\omega_R^2\vec{E}(t) \quad (3)$$

where $\omega_R^2 = \frac{e^2 n_0}{\epsilon_0 m}$ and n_0 is the maximum concentration of oscillators, ω_R is the characteristic frequency of natural oscillations of the charges, and ω_0 is the intrinsic frequency of oscillations of the charges for the maximum of absorption band. As a

rule, $\omega_0^2 = \omega_R^2 + \alpha^2$, $\alpha = \gamma$ is the attenuation coefficient. Eq. (3) is used to analyze the spectra of resonant dielectric losses. Its solution is:

$$\varepsilon^*(\omega) = \varepsilon + \frac{(\varepsilon_S - \varepsilon_\infty)\omega_R^2}{\omega_R^2 - \omega^2 + 2i\alpha\omega} \quad (4)$$

However, analysis based on the Lorentz polarization Eqs. (3) and (4) does not allow evaluation of the relaxation properties. Analysis of these characteristics is possible by the Havriliak-Negami model, which operates with Eqs. (5) and (6),^[20] showing that the radio frequency bands have different relaxation characteristics. Moreover, the relaxation characteristics differ for different sections of each line, which can be clearly seen from Figs. 4(a) and 4(c), showing the curves approximating the bands of radio frequency radiation according to Eq. (5). The approximation process provides the parameters, allowing plotting the curves of relaxation time distribution function $g(\tau)$ using Eq. (6) (Figs. 4b and 4d). The values of the coefficients $\log f_{\max}$, $\Delta\varepsilon$, a and b for the Havriliak-Negami equation, are shown in Table 1. It is clear that the distribution of relaxation time has a long tail on the high frequency side.

$$\varepsilon'' = \frac{\Delta\varepsilon}{[1 + (if/f_0)^a]^b} \quad (5)$$

$$g(\tau) = \frac{1}{\pi} \frac{(\tau/\tau_H)^{\alpha\gamma} \sin(\gamma\theta)}{[(\tau/\tau_H)^{2a} + 2(\tau/\tau_H)^a \cos(a\pi) + 1]^{\gamma/2}} \quad (6)$$

$$\text{where } \theta = \arctan \left| \frac{\sin(\gamma\pi)}{(\tau/\tau_H)^a + \cos(a\pi)} \right|.$$

It is known that inelastic deformation of partially crystalline polymers is fundamentally nonuniform throughout the volume of polymer sample.^[21] The transition from elastic (uniform) to inelastic (inhomogeneous) deformation is associated with a loss of mechanical stability of the system. In this case, the polymer acquires a regular fibrillar structure. Such fibrillation is characteristic of both crystalline and amorphous polymers.^[21–23] In other words, the loss of stability of the polymer system is accompanied by the structural self-organization of the polymer—under rapid uniaxial loading, the globular structure transforms into a more ordered fibrillar structure. Ultimately, critical fibrillation leads to a decrease in internal stresses in the system due to the localization of deformations in the form of shear bands, and then a rheological explosion occurs, accompanied by pulsed radiation of ultrasonic waves, rupture of polymer chains, and the formation of free charge carriers, radicals and defects in the form of nanopores. The next part of the article considers these processes in terms of polymer morphology.

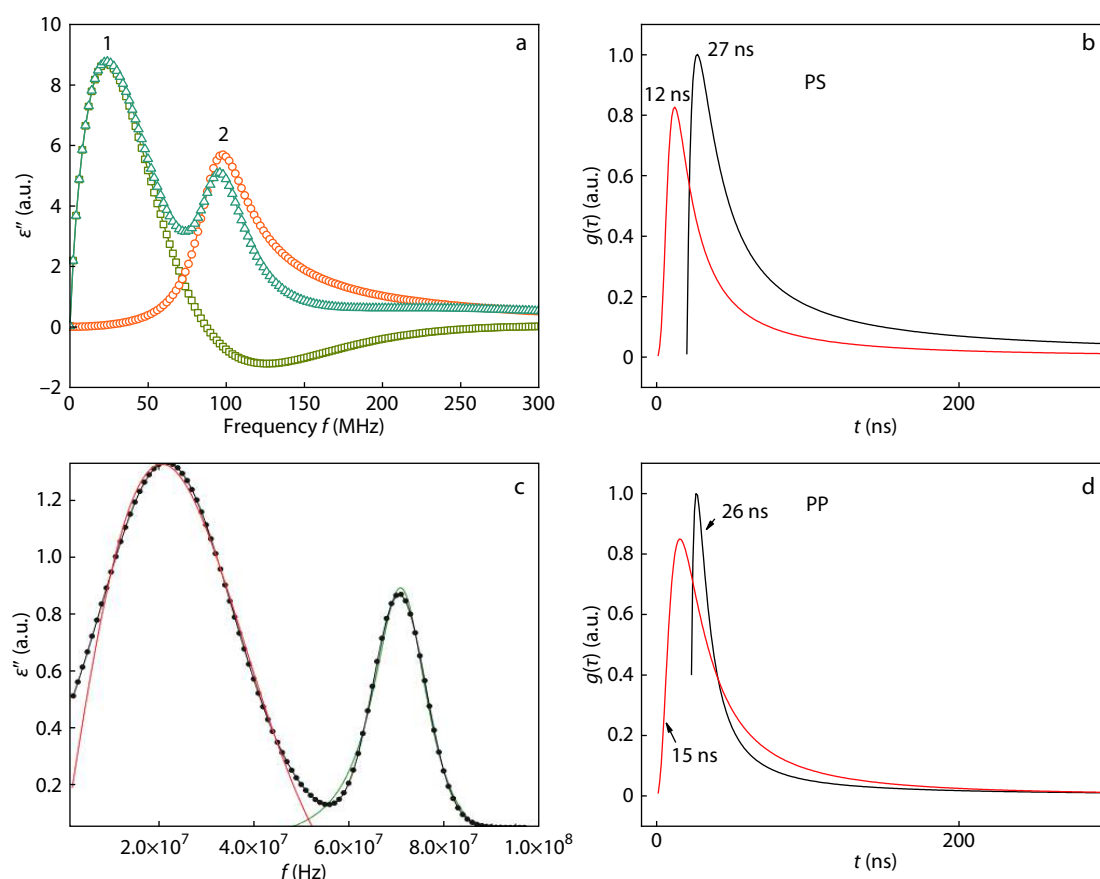


Fig. 4 Approximation of the radio frequency bands of (a) PS and (c) PP according to the Havriliak-Negami Eq. (5) and the corresponding distribution of relaxation time for (b) PS and (d) PP obtained from Eq. (6). Colors denote individual line in spectra in Fig. 3. In panels a and c, red and light green are individual lines, and dark green is total spectra.

Table 1 Parameters of the Havriliak-Negami model for radio frequency radiation bands of PS and PP.

Havriliak-Negami model	$\log f_{\max}$	$\Delta\epsilon$	a	b	$\tau_{\max}$ (ns)
PS1	8.29	12.33	0.92	8.47	12.0
PS2	8.03	2.23	1.58	1.58	27.0
PP1	7.95	1.63	0.99	5.80	15.0
PP2	7.86	0.14	1.87	1.18	26.0

Transformations of Polymer Structure

X-ray diffraction methods were used to investigate changes in the structure and morphology of polymers during deformation and rheological explosion. The experimental values of the intensity I_{exp} and the small angle X-ray scattering curves I_{reg} for PS0–PS2 samples calculated in accordance with the GNOM regularization procedure are shown in Fig. 5 in coordinates scattering intensity (I) versus wave vector (s). It can be seen that the deformed PS1 and PS2 samples scatter X-ray radiation more intensively than the undeformed PS0 sample. The appearance of such additional scattering in deformed samples can only be associated with the formation of new nanoscale regions having a density different from the average density of polymer matrix in the deformed samples. It is unlikely that under particular experimental conditions of deformation of polymer samples, such regions acquire and retain after unloading (stress relieving) a density that is much higher than the density of the initial matrix. In contrast, the formation of a porous structure (discontinuity of matrix integrity) is a common phenomenon accompanying large deformations of polymers in the solid state. Accordingly, the physics of deformation of polymers in the solid state suggests the quite reasonable assumption that the main reason for the appearance of additional small-angle scattering

in the samples is the appearance of a heterogeneous nanoporous structure in the system (a system of voids in the matrix).

According to Babinet's principle, the system of voids in a matrix scatters radiation in the same way as the system of particles in a vacuum provided that the pore density is equivalently replaced by the density of the matrix, and vice versa, the density of the matrix by the density of voids. Thus, in the following, we will characterize scattering by a system of pores in the samples, using terminology that is customary for characterizing scattering from real nanoscale particles with a nonzero density equal to the density of the polymer matrix distributed in the "void", realizing that all dimensional characteristics of such particles are characteristics of the corresponding pores. Additionally, according to the inset in Fig. 5(a), the analyzed particles do not have any preferred orientation (there is no texture), and scattering from them can be interpreted in terms of scattering from isotropic systems.

Since the intensity of small-angle scattering from polymer samples was low for such a large phase contrast (polymer-vacuum), it is logical to assume that the equivalent scattering system "particles in vacuum" is low concentrated (diluted) and, therefore, weakly scattering. Note that direct proof of this statement requires additional measurements of small angle scattering in absolute units, which is beyond the scope of this work and is planned for a further study.

Small-angle scattering by a diluted system of particles can be interpreted with minimal detail (complication) of the scattering system either in approximation of a polydisperse system of particles with a known form factor (spheres, prisms, ellipsoids of revolution, etc.), or in approximation of identical particles of unknown shape and spatial structure.^[24] In the

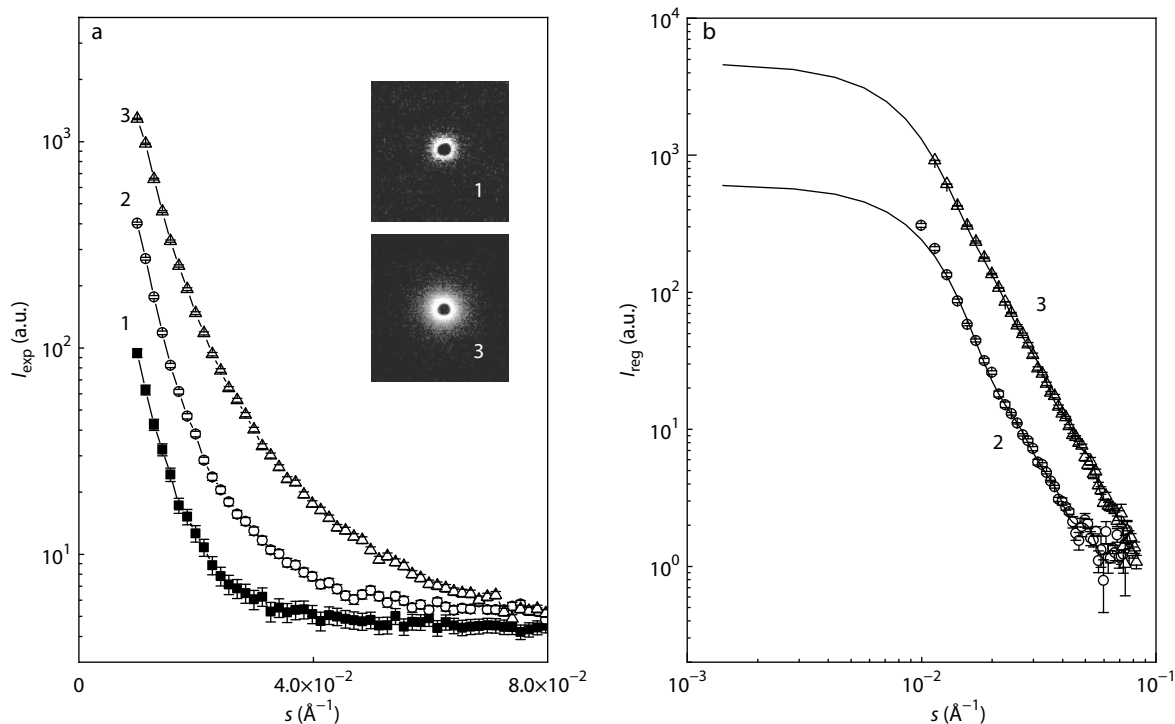


Fig. 5 (a) Experimental intensity I_{exp} of small angle X-ray scattering; (b) Small angle X-ray scattering curves I_{reg} optimized using the GNOM procedure. Samples: 1—PS0; 2—PS1; 3—PS2. The inset shows small-angle X-ray diffraction patterns of samples 1 and 3.

first case, the result of the interpretation of small-angle scattering data is the reconstructed particle size distribution function, and in the second, the determination of the shape and size of the particles.

Fig. 6(a) shows the volumetric particle size distribution functions $D_v(R)$ in the scattering approximation of the simplest model of polydisperse scattering particles in the form of spheres with radius R , calculated according to the GNOM procedure from the scattering curves of the samples.

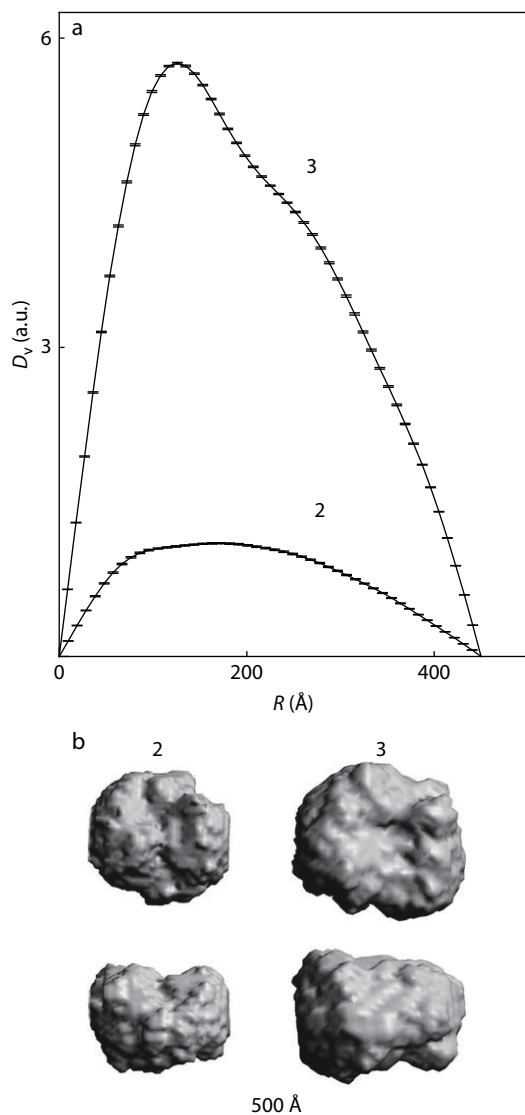


Fig. 6 (a) Volumetric size distribution functions D_v of nanopores, calculated from the scattering curves in Fig. 5; (b) The shapes of the scattering particles in the samples. The top row is a top view; the bottom row is a side view. Visualization by the model of bulk virtual ("dummy") atoms and the model of "surface accessible to solvent". Samples: 2—PS1; 3—PS2.

The functions $D_v(R)$ for the two deformed systems PS1 and PS2 are almost identical in appearance and differ only in the number of particles (pores) in the system, which increases with increasing deformation of the samples at stages I–IV of accelerated creep and fracture of the material. The values of

the particle's inertia radius R_g for samples PS1 and PS2 were also close to each other (165 and 195 Å, respectively).

In addition to calculating the volumetric particle size distribution function $D_v(R)$, in the approximation of scattering from identical particles of unknown shape and spatial structure, the shapes and sizes of such "averaged" particles were determined using the DAMMIN, DAMMIF, DAMAVER, and SUPCOMB procedures within the framework of the model of "virtual" (dummy) atoms. The possibility of restoring the low-resolution structure of polydisperse and polymorphic nano-objects from small-angle scattering data using the ATSAS software package was demonstrated previously.^[25,26]

The results of reconstructing the shape and spatial structure of the "averaged" particles are presented in Fig. 6(b). The results show that scattering "averaged" particles (pores) in polymer samples that have experienced only fast uniaxial compression (PS1) and uniaxial compression with a rheological explosion (PS2) have a shape close to the shape of a flattened ellipsoid with a ratio of maximum to minimum size approximately 1.3:1. The linear dimensions of the resulting pores in the sample after a rheological explosion (PS2) exceed the linear sizes of pores in the sample subjected only to rapid compression (PS1) by 20%, which is consistent with the relative increase in the above-mentioned radius of inertia R_g of particles for PS2 sample compared to sample PS1.

We believe that the main reason for the formation of such pores, which were observed in our experiment after unloading the sample, may be intense micros shears in the polymer volume under the action of high pressure. High local deformation of the polymer material in the zone of such microshear can cause mechanical destruction of the material and the formation of discontinuities in the matrix—"preforms" for the future porous structure, which is finally formed after the elastic recovery of the deformed matrix during stress relief (material unloading).

Additional evidence of the significant effect of shear deformations during rapid compression and rheological explosion on the change in the structure of the deformed polymer matrix was found by studying the second series of deformable samples based on semi-crystalline PP. In this case, in contrast to amorphous PS in the first series of samples, in addition to small-angle X-ray scattering method, the method of X-ray diffraction at large angles was informative.

Fig. 7 shows the diffraction patterns of samples PP0 and PP2. The diffraction pattern of the PP1 sample was almost identical to the diffraction pattern of the PP2 sample and, for this reason, is not shown in Fig. 7.

The diffraction patterns in Fig. 7 show that the test samples are partially crystalline. The diffraction patterns show that characteristic reflections of α -phase of *i*-PP with indices 130 ($2\theta=18.56^\circ$) and β -phases of *i*-PP with indices 300 and 311 ($2\theta=16.12^\circ$ and 21.31° , respectively) are present.^[27] The ratio of the intensities of reflections of the α -phase and β -phase of PP in undeformed (PP0) and deformed (PP2) samples is almost identical to each other, which indicates the unchanged phase composition of the crystalline phase of PP even under such intense mechanical stresses as a rheological explosion.

Significant changes in the diffraction pattern for deformed samples (Fig. 7) compared to the initial state include a noticeable decrease in the degree of crystallinity (amorphization of

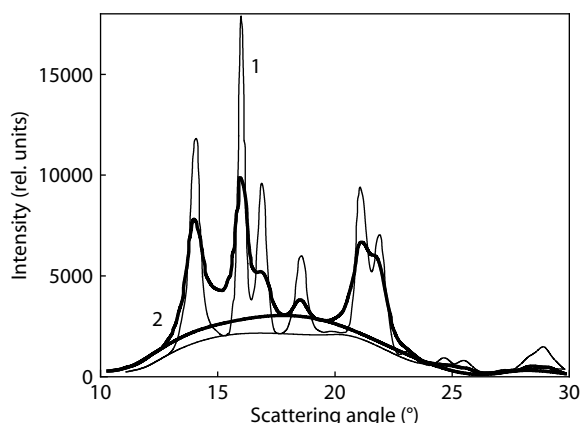


Fig. 7 Diffraction patterns of samples: 1—PP0; 2—PP2.

the material) and a significant decrease in the size of crystalline regions (crystallites) in PP, which is manifested in broadening of reflections and a decrease in their intensity.

The measured values of the degree of crystallinity of the samples with progressing deformation during rapid compression and subsequent rheological explosion were 55%, 47%, and 43% for PP0, PP1, and PP2, respectively. The crystallite sizes calculated from the half-width of the corresponding crystallographic reflections decreased by 1.8 times from PP0 sample to PP2. The reason for such significant changes in the amorphous-crystalline structure of the polymer sample at a low temperature of the deformation process can only be explained by the presence of high shear stresses, since purely normal stresses (tension, compression) cannot lead to dispersion of crystalline material (crystallites) under intense mech-

anical action on the material. This conclusion initially seems paradoxical, since in a rheological explosion experiment, the compression of a polymer sample occurs in an open volume.

Similar to PS samples of the first series, the samples of the second series also exhibit changes in polymer nanostructure under rapid compression and rheological explosion. The experimental values of the intensity I_{exp} and small-angle X-ray scattering curves I_{reg} for the samples PP0 and PP2 calculated with the GNOM regularization procedure are shown in Fig. 8, in coordinates scattering intensity (I) versus the wave vector (s). The experimental I_{exp} curves (Fig. 8) show maxima corresponding to the so-called “long periods”, characteristic of the supramolecular structure of crystalline polymers, which are due to periodic alternation of crystallites and amorphous regions in the polymer bulk. The magnitude of the large period was 147 and 80 Å for samples PP0 and PP2, respectively. Moreover, the large period in PP2 sample (after the rheological explosion) was 1.8 times shorter than in the initial undeformed PP0 sample, in full accordance with the above-described effect of crystallite size changes in the same samples. Thus, the rapid compression and subsequent rheological explosion of semicrystalline polymer lead to a sharp change (dispersion) of entire supramolecular structure of polymer as a whole.

Similar to the first series of PS samples, the additional “excess” small-angle X-ray scattering for PP2 sample subjected to rapid compression followed by a rheological explosion was attributed to scattering from the resulting porous system, analyzed by the same methods that were used for samples of the first series.

Fig. 9(a) shows volumetric particle size distribution functions $D_v(R)$ in the scattering approximation of the simplest

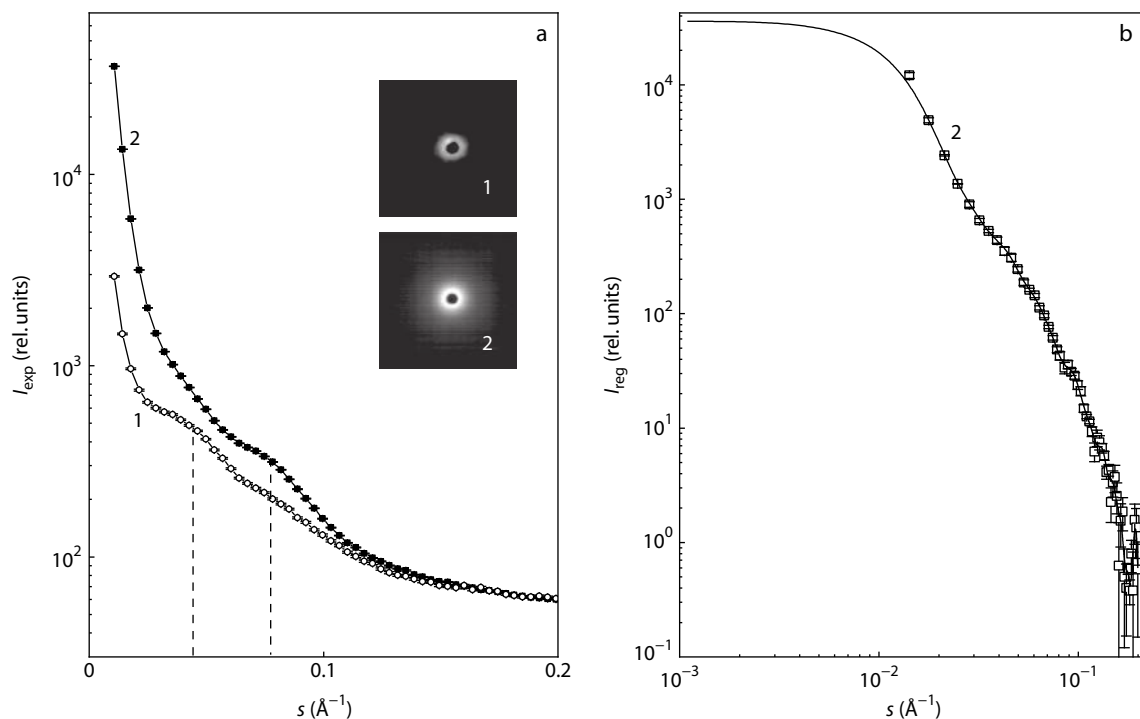


Fig. 8 (a) Experimental intensity I_{exp} of small angle X-ray scattering; (b) Low-angle X-ray scattering curve I_{reg} optimized using the GNOM procedure. Samples: 1—PP0; 2—PP2. The insets show small-angle X-ray diffraction patterns of samples 1 and 2.

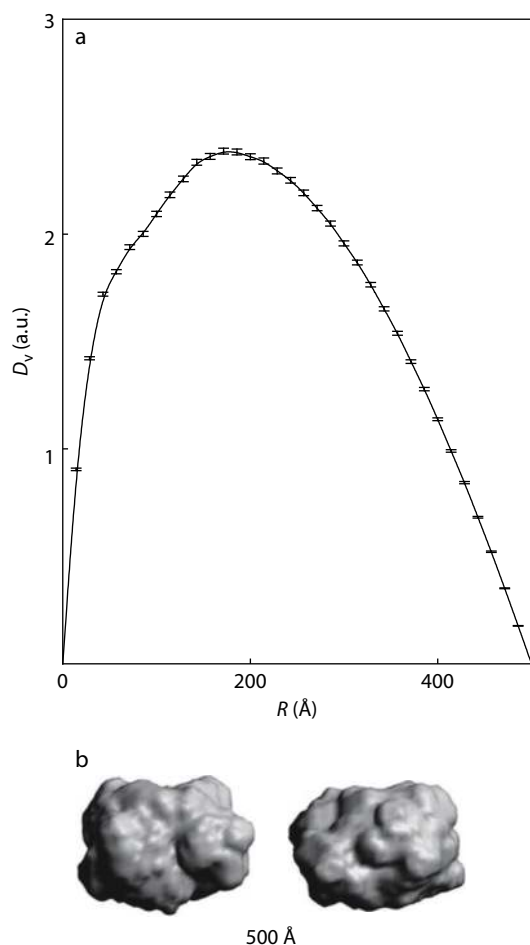


Fig. 9 (a) Volumetric nanopore size distribution function D_v , calculated from the scattering curve in Fig. 8; (b) The shapes of the scattering particles: top view (left) and side view (right). Visualization by the model of bulk virtual ("dummy") atoms and the model of "surface accessible to solvent". Sample: PP2.

model of polydisperse spherical scattering particles with radius R , calculated according to the GNOM procedure from the scattering curves of the samples. The function $D_v(R)$ for PP2 is similar to corresponding functions for PS samples of the first series. The values of the particle radius of inertia R_g for PP2 sample was 140 Å. Slightly smaller pore sizes in PP2 compared to PS2 can be explained by the greater ductility (fracture toughness) of PP matrix as compared to PS under comparable fracture conditions.

The results of reconstructing the shape and spatial structure of the "averaged" particles for PP2 are presented in Fig. 9(b). The scattering "averaged" particles (pores) in PP2 sample, which underwent rapid uniaxial compression with a rheological explosion, have a shape close to that of an elongated ellipsoid with a maximum to minimum size ratio of about 1.3:1.

The appearance of nanopores during compression and rheological explosion has a considerable effect on electrical properties and effects in polymer samples during compression. Electric charges can accumulate on the outer surface of nanopores during rapid compression and rheological explosion, making nanopores large electric dipoles inside the poly-

mer matrix. This assumption is based on the fact that the process of formation and transformation of nano- and micropores is accompanied by mechanochemical reactions and appearance of electron-hole pairs when hydrogen atom is detached from the polymer chain.^[7]

CONCLUSIONS

Summarizing the above material, we can assume that rheological explosion occurs in polymer when a critical concentration of nanopores is reached. The formation of nanopores is accompanied by the generation of electron-hole pairs ($e^- + H^+$) or hydrogen atoms H and accordingly, nanodipoles during the separation of charges on the walls of nanopores, as well as $-RO_2^*$ radicals upon addition of molecular oxygen at the site of separation of the hydrogen atom. The fusion of nanopores leads to the formation of channels through which the charge density is transferred by an electromagnetic wave and a current pulse is formed. Oscillations of spins of unpaired electron in $-RO_2^*$ radicals create an alternating magnetic field. Besides, the following factors lead to ultrafast destruction of a solid-phase polymer, a rheological explosion: (a) an alternating magnetic field; (b) polarization oscillations leading to the appearance of a radio frequency electromagnetic field; (c) free charge density. The experimental data presented in this work and the conclusions made on their basis do not contradict the concept of magnetoplastic fracture of a solid body, which recently was intensively developed by Profs. Buchachenko and Morgunov.^[28,29]

The results of the performed studies show that the main reason for the formation of pores in polymer samples in rheological explosion experiments is the intense microshifts in the polymer volume under the action of high applied pressure. It was also shown that the formation of a porous system during compression and rheological explosion occur according to some unified scheme that does not depend on whether the polymer matrix is amorphous or semicrystalline and whether it is in a glassy state or not.

For deformed PP samples compared with the initial state, there is a noticeable decrease in the degree of crystallinity (amorphization of the material) and a significant decrease in the size of crystalline regions (crystallites) in the PP, which is expressed in broadening of reflections and a decrease in their intensity.

In amorphous PS, scattering "averaged" particles (pores) in polymer samples that have experienced only fast uniaxial compression (PS1) and uniaxial compression with a rheological explosion (PS2) have a shape close to the shape of a flattened ellipsoid with a maximum to minimum ratio of about 1.3:1. The linear dimensions of the resulting pores in the sample after a rheological explosion (PS2) exceed the linear sizes of the pores in the sample subjected only to rapid compression (PS1) by 20%, which is consistent with the relative increase in the radius of inertia R_g of particles for PS2 compared to PS1.

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REFERENCES

- 1 Bridgman, P. W. Effects of high shearing stress combined with high hydrostatic pressure. *Phys. Rev.* **1935**, *48*, 825–847.
- 2 Bridgman, P. W. Flow in heavily stressed metals. *J. Appl. Phys.* **1937**, *8*, 328–336.
- 3 Meade, C.; Jeanloz, R. Acoustic emissions and shear instabilities during phase transformations in Si and Ge at ultrahigh pressures. *Nature* **1989**, *339*, 616–618.
- 4 Holzhausen, G. R.; Johnson, A. M. The concept of residual stress in rock. *Tectonophysics* **1979**, *58*, 237–267.
- 5 Sleep, N. H.; Blanpied, M. L. Creep, compaction and the weak rheology of major faults. *Nature* **1992**, *359*, 687–692.
- 6 Kanel, G. I.; Fortov, V. E.; Razorenov, S. V. Shock waves in condensed-state physics. *Phys.-Usp.* **2007**, *50*, 771–792.
- 7 Aleksandrov, A. I.; Alexandrov, I. A.; Prokof'ev, A. I.; Bubnov, N. N. Pulse mechanochemistry of organoelement compounds. *Russ. Chem. Bull.* **1999**, *48*, 1599–1614.
- 8 Aleksandrov, I. A.; Gritsenko, O. T.; Getmanova, E. V.; Obolonkova, E. S.; Serenko, O. A.; Shevchenko, V. G.; Aleksandrov, A. I. Muzafarov, A. M. Behavior of polystyrene-based nano- and microcomposites under fast compression. *Tech. Phys.* **2011**, *56*, 491–495.
- 9 Aleksandrov, I. A.; Gritsenko, O. T.; Perov, N. S.; Getmanova, E. V.; Obolonkova, E. S.; Serenko, O. A.; Shevchenko, V. G.; Aleksandrov, A. I.; Muzafarov, A. M. Fracture of polystyrene- and molecular silica sol-based nanocomposites during fast compression. *Tech. Phys.* **2013**, *58*, 88–93.
- 10 Aleksandrov, A. I.; Alexandrov, I. A.; Prokof'ev, A. I. Radio-frequency superradiance at the rheological explosion of a paramagnetic polymer composite containing manganese complexes. *JETP Lett.* **2013**, *97*, 546–548.
- 11 Aleksandrov, A. I.; Aleksandrov, I. A.; Zevin, S. B.; Degtyarev, E. N.; Dubinskiy, A. A.; Abramchuk, S. S.; Prokof'ev, A. I. Radio-frequency superradiance induced by the rheological explosion of polymer composites containing paramagnetic cobalt complexes. *Russ. J. Phys. Chem. B* **2016**, *10*, 69–76.
- 12 Aleksandrov, A. I.; Shevchenko, V. G.; Aleksandrov, I. A. Generation of superradiance by pulsed mechanical action. *Tech. Phys. Lett.* **2020**, *46*, 346–349.
- 13 Aleksandrov, A. I.; Aleksandrov, I. A.; Shevchenko, V. G. Multiferroic based on metal-organic dimers with the Dzyaloshinskii-Moriya effect. *JETP Lett.* **2016**, *104*, 568–572.
- 14 Aleksandrov, A. I.; Shevchenko, V. G.; Aleksandrov, I. A. A polymer composite based on organometallic cobalt dimers with Dzyaloshinskii-Moriya effect. *Polym. Sci. Ser. A* **2018**, *60*, 74–80.
- 15 Nielsen, L. E.; Landel, R. F. Mechanical properties of polymers and composites, 2nd ed. Marcel Dekker, Inc., NY, **1994**, p. 112.
- 16 Petoukhov, M. V.; Franke, D.; Shkumatov, A. V.; Tria, G.; Kikhney, A. G.; Gajda, M.; Gorba, C.; Mertens, H. D. T.; Konarev, P. V.; Svergun, D. I. New developments in the ATSAS program package for small-angle scattering data analysis. *J. Appl. Cryst.* **2012**, *45*, 342–350.
- 17 Tikhonov, A. E.; Arsenin, V. Y. Solutions of ill-posed problems. John Wiley & Sons, New York, **1977**, pp. 258.
- 18 Wertz, J. E. Bolton, J. R. Electron spin resonance. Chapman and Hall, New York, **1986**, pp. 500.
- 19 Lorentz, H. A. Theorien physikalischer Erscheinungen. *Physikalische Zeitschrift*. **1899**, *498*, 514–591.
- 20 Kremer F. Broadband dielectric spectroscopy, Springer-Verlag, Berlin Heidelberg. **2003**, pp. 60–98.
- 21 Volynskii, A. L.; Bakeev, N. F. *Structural self-organization of amorphous polymers* (in Russian). Fizmatlit, Moscow, **2005**.
- 22 Bendler, J. T. Conformational origin of glassy-state relaxation and ductility in aromatic polycarbonates. *Comput. Theor. Polym. Sci.* **1998**, *8*, 83–92.
- 23 Othmezzouri-Decerf J. Investigation of the low temperature ageing kinetics of glassy polycarbonate by mechanical damping spectroscopy. *J. Mater. Sci.* **1999**, *34*, 2351–2359.
- 24 Feigin, L. A.; Svergun, D. I. Structure analysis by small-angle X-ray and neutron scattering. New York: Plenum Press, **1987**, pp. 335.
- 25 Ozerin, A. N.; Kurkin, T. S.; Ozerina, L. A.; Dolmatov, V. Y. X-ray diffraction study of the structure of detonation nanodiamonds. *Crystallogr. Rep.* **2008**, *53*, 60–67.
- 26 Shtykova, E. V. Shape determination of polydisperse and polymorphic nanoobjects from small-angle X-ray scattering data (computer simulation). *Nanotechnologies in Russia*, **2015**, *10*, 408–419.
- 27 De Rosa, C.; Auremma, F. Diffraction analysis of ordered and disordered crystals. New Jersey: John Wiley & Sons, Inc., **2014**, pp. 480.
- 28 Buchachenko, A. L. Microwave stimulation of dislocations and the magnetic control of the earthquake core. *Phys.-Usp.* **2019**, *62*, 46–53.
- 29 Morgunov, R. B. Spin micromechanics in the physics of plasticity. *Phys.-Usp.* **2004**, *47*, 125–148.