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ORIGINAL PAPER

Effect of strain rate on the behavior of three-dimensional polymers of oligoesteracrylates under the conditions of the uniaxial elongation

S. M. Kireeva · Yu. M. Sivergin

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Abstract For three-dimensional polymers based on the dimethacryloil derivatives adipic and sebasinoil acids and dicarbonyloxyethylene we have established the influence of the deformation velocity (V_ε) on their behaviour under the conditions of the uniaxial elongation. With the increase of V_ε up to a distinct value of $V_{\varepsilon l}$, the ultimate stress σ_m for of the polymers grows, but at $V_\varepsilon > V_{\varepsilon 1}$ the value of σ_m decreases. This phenomenon is explained. With the rise of V_ε, the module of elasticity E_1 increases and the curves $\sigma(\varepsilon)$ are shifted to the left along the ε axis. The change of the character of the structural organization of three-dimensional polymers in the deformation process of their samples was established.

Keywords Strain rate · Three-dimensional polymers · Oligoesteracrylates · Uniaxial elongation · Morphology

Introduction

The products of different types obtained by using tetrafunctional monomers (TFMs), which form three-dimensional polymers, are supposed to have a set of properties that satisfy imposed practical requirements. In a number of works devoted to the modeling of free-radical polymerization of TFM, it is shown [1] that for the resulting three-dimensional polymers the mono- or bimodal granulometric distribution (GMD) of nanogels (an elementary structural unit in the three-dimensional polymers) is typical. The results, presented in [1], allow to propose the following scheme of the structural organization for three-dimensional polymers:

S. M. Kireeva · Yu. M. Sivergin (✉)
Semenov Institute of Chemical Physics RAS, st. Kosygina 4,
Moscow 119991, Russian Federation
e-mail: ashy47@yandex.ru

the monomer → the branched macromolecule

→ the unitary three-dimensional structural element (nanogel)

→ the microgel (the multitude of nanogels)

→ macrobody of three-dimensional polymer (the multitude of microgels).

The GMD points to the fact that in the course of three-dimensional polymerization of TFM, the nanogels with a different the degree of polymerization P_n are generated (P_n varies from several monomeric units to several hundreds and thousands of such units) [1].

The GMD is responsible for lowering the strength properties of polymers TFM due to poor binding between nanogels particles at the formation of the microgels. This is the first type of the weak connection. The second type of the weak connection is brought about at the formation of macrobody of three-dimensional polymers out of microgels. In other words, this is the connection between microgels' particles. Thus, in the macrobody of three-dimensional polymers, there exist two types of the weak connectivity between structural particles (macrodefectiveness) and defects on the molecular level of the polymer skeleton. This is an additional defect in the structure of TFM polymers, worsening the mechanical properties of the three-dimensional polymers (in the nanogels there are such defects as cycles, pendant functional groups, end groups, etc).

The complex of mechanical properties of three-dimensional polymers is determined not only by their chemical nature, but also by the character of relaxation processes occurring in them in the course of the deformation of the samples. That is why the strain–strength properties of these polymers should depend on of the strain velocity of the samples. It is necessary to state that this problem has been given little attention to by researchers [2–6].

It is known that polymeric articles work within the regimes of deformational influences with different velocities; therefore, it is important to be aware of this problem.

Our work is devoted of the investigation of the behaviour of three-dimensional polymers of oligoester(meth)acrylates in the regime of uniaxial tension at different strain velocities (V_ε). The polymer samples were prepared out of the OEA of different chemical nature. The morphology of these OEA polymers was investigated and so was investigated its variation in the deformation samples.

Experimental

Materials

The monomers 1,2-bis(methacryloiloxyethylenoxycarboniloxy)-ethylene (MEKE)

$$H_2C{=}C(CH_3)COO(CH_2)_2O{-}C(O)O(CH_2)_2OC(O){-}O(CH_2)_2OOC(CH_3){=}CH_2,$$

bis(methacryloiloxyethylenoxy)adipoil (MEA)

$$H_2C{=}C(CH_3)COO(CH_2)_2O{-}C(O)(CH_2)_4C(O){-}O(CH_2)_2OOC(CH_3){=}CH_2$$

and bis(methacryloiloxyethylenoxy)sebasinoil (MES)

$$H_2C{=}C(CH_3)COO(CH_2)_2O{-}C(O)(CH_2)_8C(O){-}O(CH_2)_2OOC(CH_3){=}CH_2$$

were synthesized by the method of non-equilibrium condensation 1-methacryloiloxyethylene-2-hydroxy (I) with bischlorformiate ethylene (II, MEKE) or dichloranhydride adipic acid (III, MEA) or dichloranhydride sebasinoil acid (IV, MES) as described in [2, 4, 6] in accordance with the scheme given below:

$$\begin{gathered}H_2C{=}C(CH_3)COO(CH_2)_2OH + Cl{-}R{-}Cl\\ \rightarrow (H_2C{=}C(CH_3)COOCH_2CH_2O)_2{-}R,\end{gathered}$$

where R is the portion between atoms O– in the formulas MEKE, MEA, MES.

The products I, II, III, and IV were obtained as commercial grade materials and then purified by distillation under vacuum. The analyses by GPC showed that these substances and MEKE, MEA, MES were better than 99% pure and are monodisperse substances. MEA and MEKE are the light yellow liquids with $n_D^{20} = 1.4684$, $\rho_{20}^{20} = 1.1347$, bromination number = 82.7 Br/100 g for MEA; $n_D^{20} = 1.4657$, $\rho_{20}^{20} = 1.228$, bromination number = 85.1 Br/100 g for MEKE. The MES is the light yellow solid product with $T_m = 331–311.5$ K.

The monolithic samples of the MEKE, MEA, and MES polymers were obtained in the casting mold (the mold allowing the preparation of six samples per operation) with an internal teflonic gasket. Before pouring the monomer, the internal surface of the mold was covered with a layer of antiadhesion polyisobutylene of rubber in gasoline. As the initiator, we used a system of cumene hydroperoxide solution V_2O_5 in the tributylphosphate. The reaction solution was poured in the mold, the processing regime included the exposure of the mold with reaction solution at $T = 298–321$ K to get the glassy state. The obtained solid samples were withdrawn from the shape, and they were treated with heat in a temperature range 373–400 K in the sand band in order to obtain the degree of conversion close to 100%. The molding specimens had the form of dumb-bells with a diameter of the working part of the sample of 5 and 40 mm long (total length of the sample being 75–80 mm).

Methods

The mechanical properties of the samples of MEKE, MEA, and MES polymers were studied on the universal machine “Instron TT-DLM” at the deformation rates $(0.03–880) \times 10^{-2}$ min^{-1}. The working base of extensometer is equal to 10 mm; the temperature of test is 298 K.

The physical structure of the block samples of the investigated polymers was studied by the electronic microscopy method on a microscope type UEMV-100B (resolving power 10 Å) by removing carbon replicas from the surface of samples of the split which were previously subjected to the oxygen etching [2, 4].

The other methodes of investigation were common ones [2, 4, 5].

Results and discussion

The effect of the deformation rate (V_ε) on the shape of the tensile-test diagrams of stretching and strain–strength parameters of MEKE, MEA, and MES polymers is shown in Fig. 1 and in Table 1. The dependence of the values ultimate stress σ_m from lgV_ε (Fig. 2) is linear (with the exception of the MEKE polymer when the deformation rate $V_\varepsilon \geq 8.7 \times 10^{-1}$ min^{-1}). According to the tangent angle of the slope of these lines, the values of velocity modulus m^* (Table 1) were calculated. The values of m^* were the smallest for the MEA polymer, i.e., in the case of the MEA polymer, the smallest dependence σ_m from V_ε takes place.

For the MEKE polymer (Fig. 2, curve 1), the dependence of strength on the deformation velocity is of the extreme character: with the increase of the deformation velocity (up to 0.87 min^{-1}) the ultimate stress increases and then sharply decreases. A similar effect can be expected for other OEA polymers, but at other values of the deformation velocity: the greater the flexibility of the polymer matrix, the higher the value of V_ε, should be at which the drop of σ_m will take place. An extremal dependence σ_m upon the rate of deformation occurs due to the relaxation nature of the fracture process of three-dimensional OEA polymers. When the load is applied to the samples two processes occur: (a) the reorientation of segments of the chains (the chains of type 1) along the axial tension, but one part of the chains remains inoperative (the chain of type 2); (b) working (stressed) parts of three-dimensional network have a certain durability τ and at $t_{\text{exp}} > \tau$ they rupture with the formation of macroradicals.

It is known that

$$\tau = \tau_o \exp(U_\text{o} - \gamma\sigma)/\kappa T,$$

where τ_o reexponential factor, U_o is the apparent activation energy of destruction, γ is the coefficient depending on of the polymer structure, σ, T, k denotes the stress, temperature, the Boltzmann constant, respectively.

Formed macroradicals either interact or leave the microvolume, in which the split of the chain take place. At low V_ε the proportion of chains of type 1 may be the maximum, but the durability factor of the chains may have a pronounced effect and the value of σ_m will decrease.

With the increase of V_ε, the competition of the phenomena changes the share in chains of types 1 and 2 and the influence of the durability conditions the growth σ_m up to a certain value of $V_{\varepsilon 1}$ for each polymer. Above this value $V_{\varepsilon\text{l}}$, the share of the effective chains of type 1 decreases and the magnitude of σ_m also starts to decrease (Fig. 2). For MEKE polymer, the value $V_{\varepsilon 1} \approx$ 0.8–0.9 min^{-1}, but at $V_\varepsilon > 0.9$ min^{-1}, the value σ_m begins to decrease significantly, reaching the magnitude of $\sigma_\text{m} \sim 11$ MPa at $V_\varepsilon = 8.8$ min^{-1} (Table 1; Figs. 1, 2).

Thus, before the process of extension, the direction of the axes of the similar segments of the part of chains coincides (or comes close to) with the direction of the axial extension. For the orientation of chains at the elongation of the samples, it is necessary to have a certain period of time. The higher the stiffness of the polymer matrix, the more time is needed for the orientation of the chains. So the time is sure to come when, from some value t_{exp} (and specific moment for each of the OEA

Fig. 1 The tensile-test diagram of the MEKE (**a**), MEA (**b**), MES (**c**), and polymers (**a**) at different extension velocities per minute. The numbers on curves correspond to V_ε, given in the Table 1

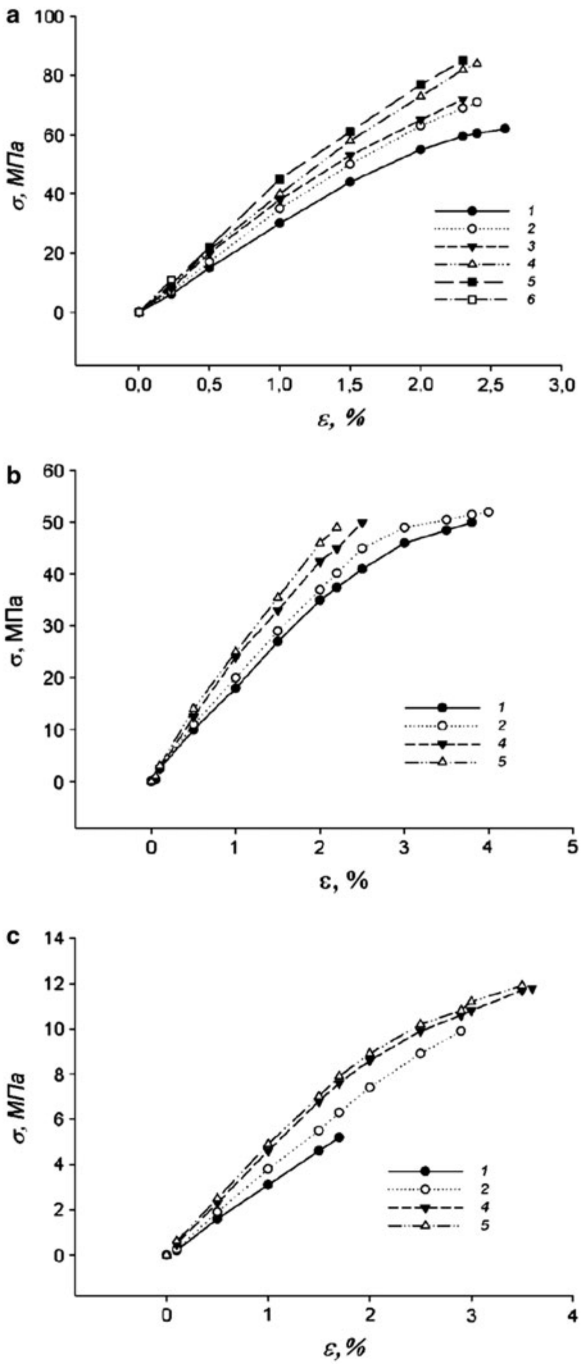

Table 1 The dependence of strain–strength characteristics, of modulus E_1 and modulus velocity m^* of samples of OEA polymers under extension upon the nature of oligomeric block and of the deformation velocity

MEKE				MEA				MES			
$V_\varepsilon \times 10^2$ min^{-1}	σ_m (MPa)	ε_m (%)	E_1 (MPa)	$V_\varepsilon \times 10^2$ min^{-1}	σ_m (MPa)	ε_m (%)	E_1 (MPa)	$V_\varepsilon \times 10^2$ min^{-1}	σ_m (MPa)	ε_m (%)	E_1 (MPa)
0.08	67	2.6	3190	0.06	50	3.8	1760	0.03	5.2	1.7	306
0.77	70	2.5	3640	0.31	52	4.0	1920	0.3	9.8	2.9	360
1.5	72	2.5	3740	–	–	–	–	–	–	–	–
7.1	84	2.4	3920	3.1	50	2.4	2120	3.2	11.8	3.5	450
87	85	2.3	4220	51	49	2.2	2140	40	12.0	3.4	460
880	11	0.2	4760	–	–	–	–	–	–	–	–
m^*	0.282			0.045				0.130			

polymer), the cites of chains would not be able to orient along of the axial of tension, and the higher V_ε (after the extremum in the in curve $\sigma(V_\varepsilon)$), then the smaller number of cites of the chains would carry the load. Ultimately, only those chains whose direction coincides with the direction of extension before the start of deformation the process might be effective. The increase the localization of the stress on the bonds with the increase in V_ε should be borne in mind. After the disruption of the bonds, the number of formed free radicals is determined by the competition of the life time free radicals and speed testing. With the rise of V_ε the removal of radicals rate increases, therewith probability of recombination of radicals with the formation of the primary chain reduces, or in other words, with the rise of V_ε the rate of crack growth increases, since bond breaking is the beginning of the formation of cracks. That is, with the rise magnitude of V_ε, the higher of $V_{\varepsilon 1}$, the value of σ_m should fall. Hence, we conclude that the determining influence on the dependence of σ_m upon V_ε has the flexibility of the polymer matrix. At very high speeds of V_ε, the orientation of structural elements and the cites of macrochains along the axial of tension is substantially lower value of the V_ε, for example, as noted above, when $V_\varepsilon = 8.8$ min^{-1} of MEKE polymer is destroyed even at $\sigma_m = 11$ MPa (Fig. 2). The ultimate values for the deformation decrease with the rise of the test speed, which is associated with a diminishing contribution of highly elastic component of deformation. The difference between the testing temperature (T_{test}) samples of three-dimensional OEA polymers and glass transition temperature T_g of these polymers is of importantance. The values of T_g for the polymers investigated are (where T_{gexp} and T_{gcalc} are experimental and calculating values T_g):

Polymer	T_{gexp}	T_{gcalc}	$T_{\text{gexp}} - T_{\text{test}}$
MEKE	408	304	110
MEA	378	294	80
MES	293	270	−5

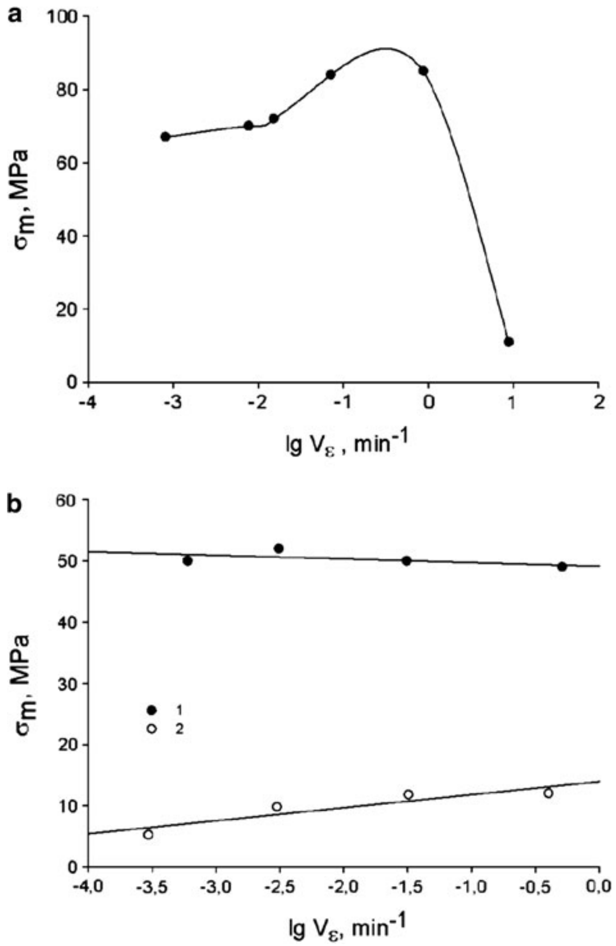

Fig. 2 The dependence of the ultimate stress of MEKE (**a**), MEA (**b**, 1), MES (**b**, 2) polymers upon the extension velocity

That is, in our case, the difference ($T_{gexp} - T_{test}$) for of the polymer MEKE is the greatest and lowest in the case of MES polymer, and this distinction is manifested in the character of stress–strain diagrams $\sigma(\varepsilon)$, in a different change of the curves $\sigma(\varepsilon)$ with the velocity V_ε, as well as in the ultimate values of σ_m and ε_m and the modulus of elasticity E_1 (Fig. 1; Table 1). The calculated values of the glass transition temperature T_{gcalc} were calculated by the method of Askadskii [6]. They point out to the correct order of their change in a number of polymers, but the distinction between T_{gexp} and T_{gcalc} substantial, reflecting the inadequacy of the calculation results with of the experiment.

The change of the deformation velocity in the given range of V_ε in the case of MEA polymer (Fig. 1b) also affects on the change in strength (Fig. 2; Table 1). Note the observed decrease, the ultimate values of elongation with the increase of the deformation velocity, which is related, as has already been indicated, with a decrease in the contribution of highly elastic component of deformation.

In the case of MES polymer (Figs. 1, 2) with the rise of the strain velocity, the ultimate values σ_m and ε_m increases. The rise of σ_m is due to the above reasons, as well as due to the fact that at low speeds V_ε has a stronger influence of the transition state of vitreous to the highly elastic state at T_{test}.

The dependence of ε_m upon V_ε (see Table 1) in the vicinity of the highly elastic state of has an increasing character. When V_ε is decreased, we observe the fall of ε_m due to the influence of the factor of chains' durability. This leads to the fact that in the case of MES polymer during the test duration, there is no chance for highly elastic component of deformation with large relaxation times to be realized.

The question arises: does the structural organization of OEA polymers influence on their behavior in terms of deformation at different V_ε? Figure 3 illustrates micrographs of the structure of MEKE, MEA, and MES polymers. It is evident that common for them is the presence of the microinhomogeneous globular structure, and morphology of structural elements and their size depends on the nature of three-dimensional of polymer, i.e., the morphology of structural formations depends on the sizes and chemical nature of the oligomeric block. For the MEKE polymer containing the carbonate groups in the oligomeric unit (Fig. 3a), partial aggregation of the primary globules is characteristic in appearance resembling anisodiametric structure (secondary structural elements). For the polymers containing only ester groups, but differing in the size of oligomeric block (the MEA and MES polymers), primary and secondary globular structures are characteristic; in the case of the MEA polymer (Fig. 3b), a globular structure with globules of size 300–400 Å are observed, for the MES polymer (Fig. 3c)—more irregular structure, characterized by the presence of not only the globules, but also more complex secondary structures is typical. It should be borne in mind that at the temperature of polymerization and tests (298 K), the MES polymer is found in the transition region from the glassy state to the high elasticity state, i.e., the formation of the primary structure of the MES polymer occurs in other conditions in comparison with the conditions the MEA polymer, in which the opportunity for greater flexibility macrochains is realized.

Compare the structural organization of the MEKE and MEA polymers, in which the length of the oligomeric block is practically identical, but the distinction lies only in that the two carbonate groups in the oligomeric block MEKE are replaced by the ester groups. It is seen that for both polymers microinhomogeneous globular structure is characteristic, but the distinction lies in the packing density of the globules, the size of structural formations and to the extent of the structural resolution due to these factors. For the MEKE polymer, there takes place the aggregation of primary globules with the formation of secondary structures anisodiametric ($d = 250$–600 Å), while for MEA primary—fine globular a structures ($d = 100$–400 Å).

As mentioned above, for the MEKE polymer sample not subjected to the deformation, the presence of a irregular globular structure is typical. Figure 4 shows micrographs of the structure of the MEKE polymer samples fractured at $V_\varepsilon = 0.071$ (Fig. 4b) and 8.8 (Fig. 4c) min^{-1}. It is evident that in the case of $V_\varepsilon = 0.071$ min^{-1},

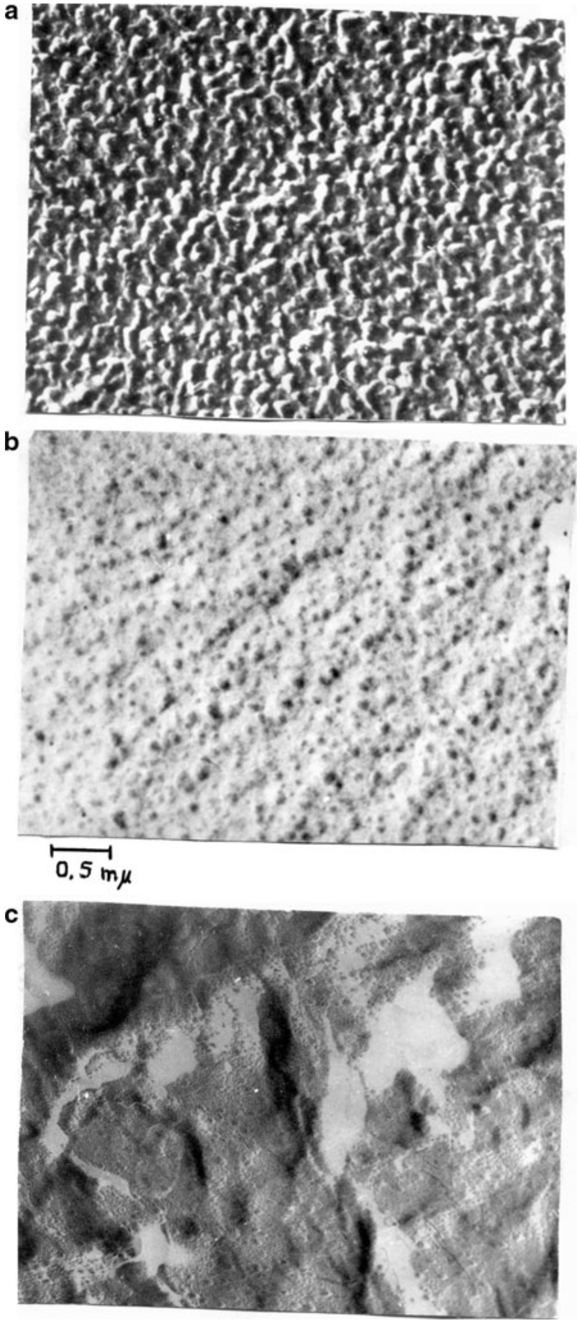

Fig. 3 The structure of the MEKE (**a**), MEA (**b**), MES (**c**) polymers. The sign “scale bar” is assigned to all the figures

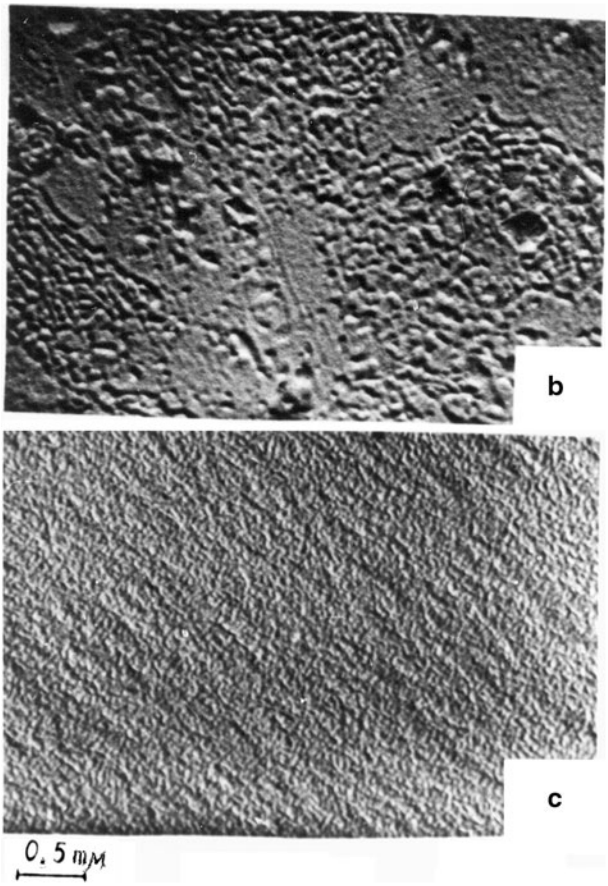

Fig. 4 The structure of the MEKE polymer samples: intact (see Fig. 3a) and destroyed at different extension velocities: 0.0071 (**b**) and 8.8 min^{-1} (**c**). The sign "scale bar" is assigned to all the figures

a noticeable change in the character of morphology takes place: there appear more aggregate formations and the zone less pronounced structure. With the increase of V_ε at two orders ($V_\varepsilon = 8.8\ \text{min}^{-1}$) (Fig. 4c), it is seen that the changes are much less and the structure resembles the structure of the original sample (Fig. 3a), but at this the strain rate the samples break when $\sigma_m = 11$ MPa, which is considerably lower than that for $V_\varepsilon = 0.071\ \text{min}^{-1}$ ($\sigma_m = 79$ MPa). Apparently, the degree of the change in the morphology of the structural elements is determined by the achieved level of deformation.

In Fig. 5, where micrographs of samples subjected to varying degrees of deformation are seen, that are already under the stretching to values of the deformation $\varepsilon = 1.5\%$ there occurs a noticeable change in the morphology of structural elements, accompanied by the aggregation of the globules; in the case $V_\varepsilon = 0.87\ \text{min}^{-1}$ (Fig. 5c) present the more sizeable structural formations are present than for $V_\varepsilon = 0.071\ \text{min}^{-1}$ (Fig. 5b), i.e., the change of the structure occurs to a greater extent. In addition to the aggregation with a further deformation (Fig. 5d), the appearance of the nidi of fracture, were observed which at the rise of deformation become even more noticeable and spread over a larger volume (Fig. 5d). The structure of destroyed samples (Fig. 5e at $V_\varepsilon = 0.87\ \text{min}^{-1}$ and Fig. 5f for $V_\varepsilon = 0.77 \times 10^{-2}\ \text{min}^{-1}$) is similar to the data given above for $V_\varepsilon = 0.71\ \text{min}^{-1}$ but a greater increase reveals distinct structural formations; as follows from Fig. 5, fine globular structure with the size of globules $d = 50$ Å is vividly observable. From the obtained data, it follows that the deformation of three-dimensional polymers is accompanied by changes in the character of the structural

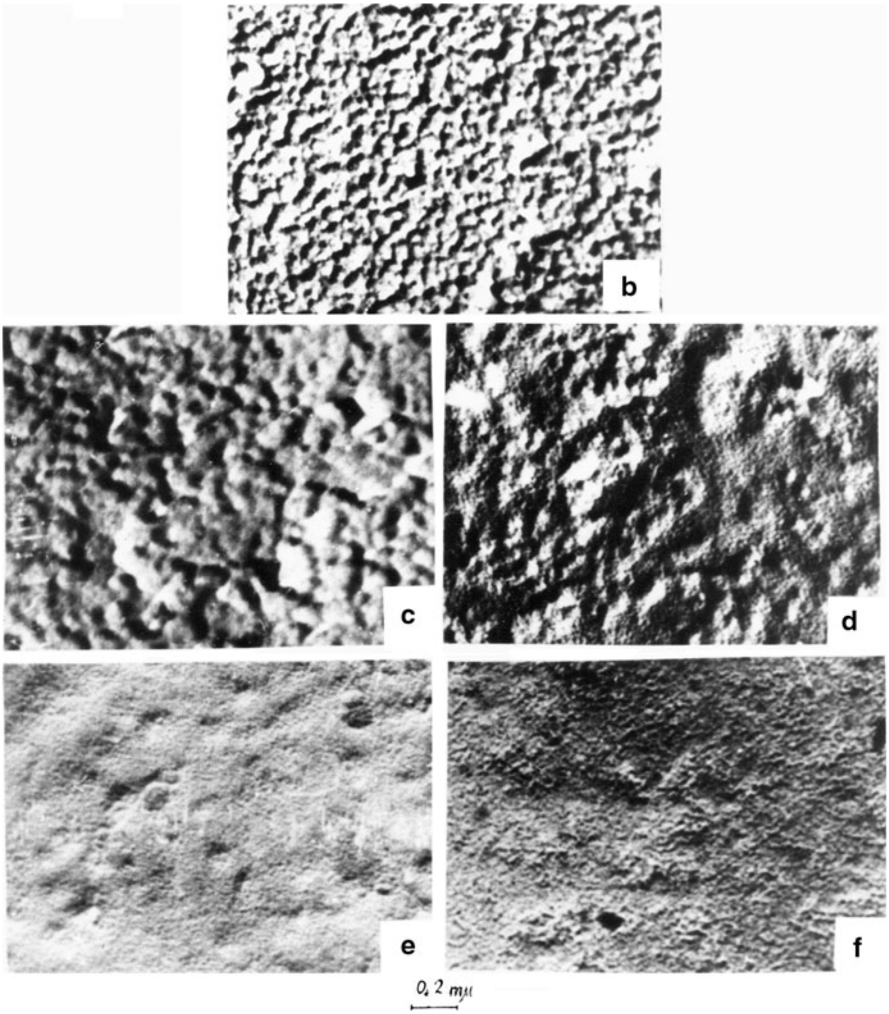

Fig. 5 The structure of the MEKE polymer samples: intact (see Fig. 3**a**), after elongation up to $\varepsilon = 1.5\%$ (**b**, **c**), $\varepsilon = 2.5\%$ (**d**) and destroyed (**e**, **f**) at different extension velocities: 0.87 (**c**, **e**), 0.77×10^{-2} (**b**, **d**, **f**) min^{-1}. The sign "scale bar" is assigned to all the figures

organization, and the fracture occurs, along interglobular bonds, which should be regarded as defects in the polymer matrix (submicrocrackes), causing the value of technical strength to be 2–3 orders of magnitude lower than compared with the theoretical prediction.

Thus, taking of three-dimensional MEKE, MEA, and MES polymers, as an example, the influence of the deformation velocity of the samples in the regime of uniaxial tension on the character of the tensile-test diagram has been proved and explained. The behaviour of OEA polymers depends not only on the chemical nature and degree of cross-linking of three-dimensional OEA polymers, but also on the state in which the polymer is found (determined by the difference in ($T_{\text{test}} - T_g$)), and structural organization of the OEA polymers.

Conclusion

(a) For the three-dimensional OEA polymers, an extremal dependence of the limited stress on V_ε was established; when V_ε rises, the elasticity module for the OEA polymers increases; the behavior of the limited deformation ε_m from V_ε is determined by the polymer rigidity (for example, in the case of a flexible MES polymer the value of ε_m decreases with the fall of V_ε).

(b) For the three-dimensional OEA polymers, an irregular morphology was established; the character of their structure changes in the course of deformation OEA polymer samples.

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