A method is proposed for obtaining uniaxially oriented specimens of amorphous unfractionated polymer with a particular oriented chain length. The length of the oriented chains and their molecular weight $M_c$ depend importantly on the conditions under which the polymer is stretched. It is shown that the strength of specimens obtained by stretching at constant $M_c$ increases linearly with the relative fraction of oriented phase. The slope of this linear relation increases with the length of the oriented molecular chains. The ratio of the maximum strength of fully oriented polystyrene to the strength of the unoriented material is found to be 78 instead of the value of 6 given in [5].

It is known that the mechanical strength of polymers is much increased if their macromolecules are first oriented in the direction of the tensile load. In ordinary unfractionated polymers there are molecules of different lengths or molecular weights. Therefore, it is important to investigate the dependence of polymer strength not only on the mean degree of orientation of the molecules but also on the nature of the oriented molecules. It is not possible merely by stretching to obtain a polymer in which molecules of different lengths are equally well oriented. In the presence of weak molecular interaction (high polymer temperature), the distances apart, and stretching the polymer leads to orientation of the chains of the molecular network, which are only part of the large molecules. The molecules whose molecular weight is less than that of a network chain ($M_c$) will then be in the folded equilibrium state. In the presence of strong molecular interaction (low temperatures, dense molecular network), the other hand, stretching results in orientation of the short segments of the molecular network. In this case, only molecules with a low molecular weight can be oriented completely. The larger molecules will be mainly in the folded state, although short segments may be oriented.

The structure of a uniaxially oriented rigid polymer can be represented as a composite material consisting of a truly amorphous phase in which are embedded straight segments of molecules with a length corresponding to a certain $M_c$. The axes of the oriented molecules coincide with the direction of stretch. To ascertain the possibilities of orientational hardening of actual polymers, it is necessary to establish:

1) the way in which the strength of a rigid polymer depends on the volume fraction of oriented molecules of a certain length;
2) the nature of the same dependence for oriented molecules of other lengths.

We have investigated these questions with reference to two uniaxially oriented linear polymers: polyvinyl acetate (PVA) and polystyrene (PS).

**Method.** The difficulty of obtaining oriented specimens containing a certain number of completely stretched molecules of strictly determined length is obvious. The problem is that the chains of the molecular network are oriented by stretching the polymer, but this is accompanied by a change in the molecular weight of the network chain $M_c$, rotation of the chain in the direction of stretch and an increase in its length.

Our earlier investigations of PS and other amorphous polymers showed [1,2] that the molecular weight of the stressed chain $M_c$ increases with the temperature of the specimen ($T$), the time it remains in the stressed state ($t$), and the stretch ratio ($L$); thus,

$$M_c = M_c(T, t, L).$$

In this equation, $M_c(T, t, L)$ is the molecular weight of the network chain at any glass transition temperature ($T_g$). For PS, $M_c(T = 100^\circ C) = 1500$, and $T_g = 100^\circ C$. The quantities $b$, $t$, and $L$ are constants whose physical significance was examined in [2].

For PS, $b = 35 \times 10^5$ $K$, $t = 3 \times 10^{-2}$ sec, while $b$ depends on the molecular weight of the polymer. For the PS discussed in this paper $M = 2 \times 10^5$ and $b = 0.27$. $L = l/l_0$, where $l_0$ and $l$ are the lengths of the original and the stretched specimen.

To obtain specimens with a constant value of $M_c$, it is necessary to vary the parameters $T$, $t$, and $L$ so that the multiplier in brackets on the right-hand side of Eq. (1) remains constant. At other values of this multiplier, the specimens obtained have another $M_c$. Fortunately, the parameters $T$, $t$, and $L$ have quite different effects on $M_c$. Thus, $M_c$ increases 200 times as the temperature $T$ rises through $100^\circ C$, 16 times for $T = 10^\circ C$, and only 3.5 times for $L = 10$.

We tried to conduct the stretching at sharply different temperatures. In this case, the values of $M_c$ were changed by tens of times. At the same time, we were able to obtain specimens with a constant value of $M_c$ and different degrees of orientation of the molecules.

Values of $M_c$ for the principal specimens of PS and PVA investigated are presented in the table.

The length of the network chain in the equilibrium state before stretching is determined by the mean square distance $\overline{s^2} = n \sigma^2$ between chain ends, where $n$ is the number of freely articulated segments of the same length $s$ in the chain. The ratio of the lengths of the equilibrium chains for two specimens is equal to $(M_c/M_c')^{1/2}$. When a specimen is stretched and the degree of orientation raised to the maximum, the equilibrium chains are both rotated in the direction of stretch and extended to the maximum length $r = ns$. Both the equilibrium and the maximum chain lengths in different specimens differ the more strongly, the greater the difference in their $M_c$. Therefore, the increase in the fraction of oriented phase in a specimen stretched at $M_c = \text{const}$ can be alternatively represented: 1) as an increase in the number of oriented network chains of maximum length, and 2) as an increase in the chain length to the maximum value. Obviously, the first case is preferable as far as we are concerned, since the requirements relating to structure formulated in the introduction will then be satisfied.

### Table

<table>
<thead>
<tr>
<th>$M_c$, 10$^5$</th>
<th>PS</th>
<th>PVA</th>
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<tbody>
<tr>
<td>0.6</td>
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<tr>
<td>1.2</td>
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The specimens were prepared as follows. The PVA was processed to form film 0.1 mm thick, from which paddle-shaped test pieces (gauge length 5 mm, width 2 mm) were cut. The PS test pieces took the form of fibers 1 mm in diameter. These test pieces were stretched at a certain temperature $T$ for a certain time $t$ by attaching a constant load. Then they were cooled rapidly under load to room temperature. In this process the high-elastic deformation and degree of molecular orientation produced by stretching were "frozen in." After cooling, the load was removed and the length and width of the test piece were measured; the modulus of elasticity (corresponding to the test conditions) and the birefringence $(\Delta n)$ were also determined. The birefringence served as a measure of the degree of orientation of the molecules.

For PS the maximum birefringence $\Delta n = -0.16$, which corresponds to total orientation of the molecules and an orientation factor equal to unity, is known [3]. Therefore, the ratio $\Delta n/\Delta n|_0$ is a measure of the orientation of the molecules of the PS specimens expressed directly in units of the orientation factor $f$.

From the modulus of elasticity and the ratio $\Delta n/(l^2 - l^4)$, we determined the number of chains $(N_c)$ of the molecular network under the test conditions. The molecular weight of the network chain was determined as $M_c = (N/N_c)p$, where $p$ is the density of the polymer, and $N$ is Avogadro's number. After this, the specimens were divided into groups with constant $M_c$. The specimens were tested on a tensile testing machine at temperatures of 20 and $-195^\circ C$. The strain rate was 100% per minute. It should be noted that the formation of "silver" during stretching and additional stretching of the specimens in the tensile tests sharply reduce the tensile strength and complicate the analysis of the experimental data. Therefore, we tried to obtain data only on undistorted specimens, i.e., without silver and additional stretching in the rigid state.

The PS specimens satisfied these conditions [4]. The PVA specimens, however, exhibited additional stretching at stresses close to the breaking stress, in spite of being tested at the temperature of liquid nitrogen. For this reason, the breaking stresses for PVA are assumed to be those corresponding to a marked departure from proportionality between the applied load and the strain. This point is easily registered on the testing machine.

**Results of the measurements and discussion.** In Fig. 1 we have plotted along the ordinate axis the relative orientational hardening $\sigma = \sigma/\sigma_0$ of PS specimens tested at $-195$ and $20^\circ C$, along the axis of abscissas the relative birefringence or orientation factor. The strength of the unoriented specimens $\sigma_0 = 6.5$ kgf/mm$^2$ at $-195^\circ C$ and 4.3 kgf/mm$^2$ at $20^\circ C$. The analogous data for PVA are presented in Fig. 2, with the difference that the breaking stresses correspond to a single temperature ($-195^\circ C$) and the values of the birefringence along the axis of abscissas are not in relative units. For PVA $\sigma_0 = 8.3$ kgf/mm$^2$. The lines 1, 2, and 3 correspond to the molecular weights of the network chain indicated in the captions. For specimens with a constant $M_c$, there is a linear dependence of strength on the orientation factor or the relative fraction of oriented phase. This dependence is expressed by the equation

$$\sigma = \sigma_0 (1 + \alpha f),$$

in which $f$ is the orientation factor.

The slopes of the straight lines or the coefficients $\alpha$ in Eq. (2) are the greater, the greater $M_c$ or the length of the oriented molecules in the specimen. Given the same orientation, the strength is greater for the specimen whose network chain has the higher molecular weight.

The straight lines in Fig. 1 can be extrapolated to large values of the orientation factor and also to $f = 1$. Maximum orientation corresponds to the state in which all the molecules, long and short, are oriented in the direction of stretch. As already pointed out, this state cannot be obtained by stretching the polymer. This, however, is not important as far as our particular problem is concerned. What is important is the fact that each straight line in Fig. 1 corresponds to a polymer oriented as a result of stacking molecules of approximately constant length. This makes it possible to extrapolate beyond the experimentally realizable degrees of orientation and, in particular, to $f = 1$. For this ideal state of the polymer,

$$\sigma_{\lim} = \sigma_0 (1 + \alpha),$$

i.e., the limiting strength is also greater for those ideally oriented specimens with long molecules.

The reciprocal of $M_c$ characterizes the number of ends of oriented molecules. The strength of fractionated unoriented polymers decreases linearly with increase in the number of ends [5]. Our data show that the strength of oriented unfractionated polymers decreases with the number of ends of oriented network chains.

In Fig. 3 we have plotted $M_c$ along the axis of abscissas and $\sigma_{\lim}$ along the ordinate axis for specimens of PS. The dashed line was constructed from

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*Since in what follows we consider the rigid state of the oriented polymer, we are not interested in the ends of the molecules and the network chains, and we call the oriented network chains oriented molecules with molecular weight $M_c$. 

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![Fig. 1. Relative hardening of PS as a function of the orientation factor. M_c: 1) 1.4 · 10^5; 2) 1.2 · 10^5; 3) 6 · 10^5; 20°C (●); −195°C (○).](image)

![Fig. 2. Relative hardening of PVA as a function of the birefringence. M_c: ○−2·10^5; □−5·10^5; −2.5·10^5; △−1·10^5.](image)