On the assumption that the performance of polymeric materials can be predicted only on the basis of long-time tests under conditions similar to those that obtain in practice, the authors consider creep, stress relaxation, and dynamic measurements at various temperatures and frequencies. Theoretical methods of estimating the life of polymeric materials are investigated with allowance for changes in the physical and chemical structure of the polymer and the nonconstancy of the activation energy of the relaxation processes over a broad temperature interval.

The behavior of polymer products in actual service is determined to a considerable extent by the physical properties of the polymer, which depend on its structure and vary with time as a result of physical or chemical processes. In the presence of stresses, physical processes are more important [1]. Chemical processes involve the degradation or crosslinking of the polymer macromolecules, whereas physical processes affect the secondary supermolecular structure. Thus, in order to neutralize undesirable chemical processes, chemical stabilization techniques are employed (introduction of antioxidants and truly soluble inhibitors in the form of colloidal particles). Since when polymeric materials operate (or are stored) under stress the supermolecular structure changes, it is important to develop methods of stabilizing the most favorable structures distinct from the above-mentioned methods of chemical stabilization [2].

Standard short-time methods of testing plastics do not give reliable estimates of product life, since the rate of relaxation and the deformation associated with structural changes at the molecular and supermolecular levels exceed the rate of change of the macroscopic physical quantities. Since polymeric materials are intended to serve for long periods, it is necessary to employ long-time testing methods capable of determining their mechanical relaxation characteristics. This can be achieved by studying the creep [3], stress relaxation [4], and dynamic properties of plastics both for various simple kinds of deformation and in complex states of stress [5]. However, the determination by these methods of the variability of the mechanical properties of polymers over a period comparable with the service life is very difficult. For this reason it is necessary to develop experimental and theoretical means of speeding up the determination of the guaranteed life under service conditions. In order to determine the guaranteed service (or shelf) life of plastics it is necessary to employ accelerated methods of estimating their physical and chemical aging from the change in mechanical properties under conditions much more rigorous than those usually encountered in service (or storage). To ensure the reliability of the accelerated methods, their data must be compared with the data of ordinary long-time tests. During service (or storage) plastics may be exposed to the action of mechanical and temperature fields, liquid aggressive media, atmospheric oxygen, and radiation, that is, factors capable of causing crosslinking (or degradation), rearrangement of the macromolecules, and modification of the supermolecular structures with resulting changes in the mechanical properties of the material.

Since it has not yet been finally established that the structural changes accompanying artificial and natural aging are identical, it is desirable to conduct parallel tests by the long-term method under service conditions and by an accelerated method under more rigorous conditions. In this case, in order to predict...
the behavior of plastics in mechanical fields, it is also important to employ theoretical methods of estimating their performance characteristics. In [3], in connection with the creep of plastics under various constant loads, it was shown that in \( \log D - \log t \) coordinates, segments of straight lines are obtained (the same is true of semi-logarithmic \( D - \log t \) coordinates, if the true stresses \( \sigma = F/S_t \) are fixed), by continuing which it is possible to predict the values of the deformation.

It also disregards the physical and chemical structural changes that undoubtedly take place at large deformations during the creep process. Since in the case of physical and chemical aging the internal stress relaxation rates associated with structural changes are essentially different, it is desirable to consider the two processes separately.

We shall start with the case of physical aging. In order to be able to estimate the variability of the mechanical properties of polymeric materials during service, it is necessary to be able to calculate the relaxation spectrum \( H(\tau) = H(\ln \tau) \). Using the spectrum \( H(\tau) \), within the framework of the theory of linear viscoelasticity we can calculate over a broad temperature-time interval the various mechanical characteristics determined both from creep and stress relaxation tests and from dynamic measurements. The justification for applying the theory of linear viscoelasticity to rigid polymers consists in the fact that, in general, plastics are used as structural materials operating at small strains, when the shape of the part and its dimensions remain practically unchanged.

In order to calculate the relaxation \( H(\tau) \) and retardation \( L(\tau) \) spectra, which are related by a well-known expression [5], it is necessary to know how the variation of the static and dynamic mechanical quantities over a broad range of times and frequencies. Since obtaining the corresponding experimental relations is a very difficult technical problem and sometimes simply impossible (under certain temperature and load conditions), it is necessary to employ the method of reduced variables [5]. The practical application of this method to amorphous and crystalline polymers with three-dimensional structure in constant and variable mechanical fields is described in [6, 7]. The essence of the method consists in the following. The creep curves (Fig. 1a), the stress relaxation curves (Fig. 2a), and the dynamic characteristics (Fig. 3a, c) are recorded at different temperatures within a given physical state on limited time and frequency intervals. Then, by shifting the corresponding curves relative to a selected reference curve along the time or frequency axis, one obtains generalized creep (Fig. 1b) and stress relaxation (Fig. 2b) curves and dynamic characteristics (Fig. 3b, d), which make it possible to obtain information about the values of the corresponding mechanical characteristics over a broad time interval. The graphical reduction operation is equivalent to multiplying the corresponding quantities by the shift factor \( \alpha_T = \frac{T_p \rho_p}{T_p \rho_p} \) (here, \( \rho_p \) is the density of the polymeric material at the reference temperature \( T_p \)) provided that the physical structure of the polymer does not change. In this case for the deformability (compliance) \( D \), the static modulus \( E \), and the components of the complex dynamic modulus \( E' = E' + iE'' \) we have the following relations:

\[
D(ta_T) = \frac{T_p \rho_p}{T_p \rho_p} \int_{-\infty}^{\infty} L(ta_T) (1 - e^{-t\tau}) d \ln \tau_p ;
\]

\[
E(ta_T) = \frac{T_p \rho_p}{T_p \rho_p} \int_{-\infty}^{\infty} H(ta_T) e^{-t\tau} d \ln \tau_p ;
\]

\[
E'(\omega a_T) = \frac{T_p \rho_p}{T_p \rho_p} \int_{-\infty}^{\infty} \frac{H(\omega a_T) \tau_p}{1 + (\omega a_T)^2 \tau_p^2} d \ln \tau_p ;
\]

\[
E''(\omega a_T) = \frac{T_p \rho_p}{T_p \rho_p} \int_{-\infty}^{\infty} \frac{H(\omega a_T) \tau_p}{1 + (\omega a_T)^2 \tau_p^2} d \ln \tau_p ;
\]