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Abstract

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KINETICS OF THE MECHANICAL DESTRUCTION OF HIGH POLYMERS

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The rupture of macromolecules of high polymers under various kinds of mechanical action is the most specific destructive process, associated precisely with the large dimensions of macromolecules. The free macroradicals formed upon rupture under the action of mechanical forces, in the absence of acceptors, are capable of undergoing the most varied typical recombination transformations, with the formation of branchings, cross-linked structures, copolymers, etc. In the presence of active acceptors, for example atmospheric oxygen, the macroradicals can be stabilized, which gives the effect of destruction; it is precisely this particular case that is considered in the present communication.

Modern practice in the processing of high polymers either makes use of rupture or encounters the necessity of taking it into account during the mechanical treatment of polymers. Yet, despite the enormous theoretical and applied significance of mechanical destruction, it has been studied only in a small number of special cases and chiefly for narrowly applied purposes (1–3). Recent work (4–6) testifies to the possibility of extending the field of use of this phenomenon in the practice of polymer processing and in the design of a number of original processes. However, the absence of systematic investigations of the dependence of the destruction process on the chemical nature of the polymer, external conditions, etc., made it impossible to draw any generalizations, even as a first approximation. This served as the reason for our undertaking a detailed investigation of the features of the process of mechanical destruction of a wide range of carbon-chain and heterochain polymers as a function of the medium, temperature, and other factors, with the aim of revealing certain general regularities of this process.

To carry out destruction in various liquid as well as gaseous media, a variety of apparatus, including original apparatus, was used, making it possible to conduct the process under strictly controlled conditions.

In the present communication, a general experimentally substantiated quantitative evaluation of the process of mechanical destruction of a number of polymers is set forth.

Figure 1 shows curves of the change in molecular weight of various polymers as a function of the time of destruction in a ball mill in a nitrogen atmosphere at $T = -10°$. The course of the curves shows that with time the molecular weight of the destruction products tends toward a certain limit, the magnitude of which is probably determined by the ratio of the energies of the chemical bonds of the main chain and of intermolecular interaction. The probability of chain rupture and the limit determined by this ratio can be calculated (7), though only very approximately, since at present we do not have sufficient data for the quantitative accounting of the micro- and macroheterogeneities of polymers.

Practically acceptable values of the destruction limit can be obtained from experimental kinetic curves $M = f(\tau)$ by graphical extrapolation to an infinite destruction time, as is shown in Fig. 2.

For the polymers we investigated, the values of the mechanical-destruction limit M_∞ are of the following order: polyvinyl acetate 11000, acetylcellulose 10000, polymethyl methacrylate 9000, polystyrene 7000, polyvinyl alcohol 4000.

Hence, whereas the limit of chemical or thermal destruction may be not only the monomer but even the products of its cleavage, the limit of mechanical destruction is a chain fragment whose magnitude, other conditions being equal, is a function of the chemical nature of the polymer. This fragment M_∞ is not directly related to the magnitude of the mechanical segment of the given polymer, since it depends on the specific conditions under which the process of mechanical cracking is carried out. In all probability, the limit for each polymer in the general case depends not only on its chemical nature, but is also a function of the temperature, the medium, and the frequency of the mechanical action. This characteristic feature of mechanical destruction, distinguishing it from other types, was observed for all polymers investigated up to the present time.

Fig. 1. Kinetic curves of mechanical destruction of various polymers: 1 —polymethyl methacrylate; 2 —polyvinyl acetate; 3 —polyvinyl alcohol; 4 — polystyrene; 5 —acetylcellulose.

Analyzing the course of the kinetic curves in Fig. 1 and taking into account the value of the destruction limit, we were able to establish, by the method of successive approximations, that the curves can be well described by the equation

$$M_\tau = Ae^{-k\tau} + M_\infty,$$

where $A = M_0 - M_\infty$; M_τ is the molecular weight at the moment τ; τ is the destruction time; M_0 is the molecular weight before destruction; k is the destruction rate constant.

The values of the constant k for the polymers investigated proved to be: polymethyl methacrylate 0.1200, polystyrene 0.0945, polyvinyl acetate 0.0468, polyvinyl alcohol 0.0237.

Such a ratio of the constants may, in a first approximation, be justified by the difference in chain rigidity and in the packing density of these polymers.

Fig. 2. Scheme for determining the destruction limit M_∞ from experimental kinetic curves. Polystyrene, $t = 10^\circ$ in air.

Equation (1) can be obtained from theoretical considerations if the concept of a destruction limit is used. If it is assumed that the probability of chain scission, and consequently the rate of destruction, are proportional to the number of possible acts of scission between fragments equal to M_∞, then

$$\frac{-d\left(\frac{M_\tau - M_\infty}{M_\infty}\right)}{d\tau} = k\frac{M_\tau - M_\infty}{M_\infty}.$$

Separating the variables, after integration and transformation we obtain equation (1). This equation only in its outward form resembles the kinetic equation of a first-order chemical reaction. It is valid for the given polymer and the specific conditions of the process, if one assumes that M_∞ is the smallest kinetic unit split off during mechanical "depolymerization."

Fig. 3. Comparison of experimental (lines) and calculated (points) values of molecular weight at various durations of destruction: 1 —polystyrene; 2 — polyvinyl acetate.

Such is the general picture of the process of mechanical destruction of amorphous glassy polymers. Naturally, the values of the constants of the equation depend on the specific conditions under which the process is carried out—the temperature, the medium, the intensity of the mechanical action, etc.—and may be used for calculating the process under those conditions for which they have been determined.

In this case the experimental and calculated values of the molecular weight as a function of the time of destruction are in very good agreement, as follows from Fig. 3.

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Note: Figure translations are in progress. See original paper for figures.