ON THE MOLECULAR WEIGHTS OF POLYMERS OBTAINED IN THE CATIONIC POLYMERIZATION OF TRIOXANE

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE MOLECULAR WEIGHTS OF POLYMERS OBTAINED IN THE CATIONIC POLYMERIZATION OF TRIOXANE

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The molecular weight of a polymer is an important characteristic that makes it possible to draw certain definite conclusions about the kinetics and mechanism of the polymerization process.

At present, only scant information is available on the dependence of the molecular weight of a polymer obtained from trioxane on various changes in the polymerization system (^{1}). In the present work, the dependence of the molecular weight of the polymer obtained in the polymerization of trioxane on the monomer concentration and on the degree of completion of the reaction was studied.

Fig. 1. Dependence of the molecular weight of the polymer on the concentration of trioxane. **a**—in methylene chloride at 30° at a conversion depth of 35-40%, $C_{\mathrm{SnCl_4}} = 4 \cdot 10^{-3}$ mol/l. **b**—in nitrobenzene at 30°, at a conversion depth of 70-80%, $C_{\mathrm{SnCl_4}} = 2 \cdot 10^{-3}$ mol/l.

The polymerization was carried out in solutions of methylene chloride and nitrobenzene at 30° under the action of tin tetrachloride. To determine the molecular weight of the polymers obtained, a viscometric method was used. The viscosity of polymer solutions in dimethylformamide was measured at 150°. The molecular weight was calculated by the formula (^{2})

$$[\eta] = 4.4 \cdot 10^{-4} M^{0.66}.$$

As can be seen from Fig. 1, there is a linear relationship between the initial concentration of trioxane in solution and the molecular weight of the polymer obtained, both in methylene chloride (Fig. 1a) and in nitrobenzene (Fig. 1b).

An analogous dependence (Fig. 2) is also observed between the degree of completion of the reaction (at constant trioxane concentration) and the molecular weight of the polymer (in both solvents).

By definition,

$$\overline{P} = \frac{\displaystyle\int_0^t (dM/dt)\,dt}{\displaystyle\int_0^t (dP/dt + dR/dt)\,dt},$$

where R denotes growing polymer chains, and P inactive polymer chains. For sufficiently large t, the integral in the numerator is equal to the consumption of monomer, i.e., ΔM; the integral in the denominator, if there is no chain-transfer reaction, is equal to the number of active polymerization centers or to the initial initiator concentration C_0. Thus,

$$\overline{P} = \frac{\Delta M}{C_0} \quad \text{or} \quad \overline{P} = \frac{M_0 \alpha}{C_0},$$

where M_0 is the initial monomer concentration and α is the degree of completion of the reaction. Since $\overline{M}_n = m_0 \overline{P}$, where $\overline{M}_n$ is the number-average molecular weight and m_0 is the molecular weight of the monomer unit, the tangent of the angle of inclination of the straight line in the coordinates $\overline{M}_n$–M_0 will be

$$\operatorname{tg}\varphi = \frac{m_0 \alpha}{C_0},$$

and similarly, for a straight line in the coordinates $\overline{M}_n$–α,

$$\operatorname{tg}\varphi = \frac{m_0 M_0}{C_0}.$$

Fig. 2. Dependence of the molecular weight of the polymer on the depth of conversion.
a—in methylene chloride at 30°, $C_M = 6.6$ mol/l and $C_{\mathrm{SnCl4}} = 4 \cdot 10^{-3}$ mol/l;
b—in nitrobenzene at 30°, $C_M = 2.9$ mol/l, $C_{\mathrm{SnCl4}} = 1.4 \cdot 10^{-3}$ mol/l.

By a special calculation it can be shown that, in the case where there is no loss of active polymerization centers, all of them participate in the reaction, and there is no chain-transfer reaction, then

$$\frac{\overline{M}_w}{\overline{M}_n} = 1,$$

where $\overline{M}_w$ is the weight-average molecular weight. If this is so, then the values of the molecular weights of the polymers determined experimentally and calculated from the initial data, or, what is the same, the values of the tangents of the angles of inclination of the straight lines calculated and obtained from experiments, should be

close. This is indeed the case. The noted regularities are characteristic of polymerization proceeding by the "living polymers" type. This allows us to suppose that the polymerization of trioxane also belongs to a type of reaction that is quite rare for a cationic mechanism. A similar linear dependence between the molecular weight of the polymer and the monomer/catalyst ratio was obtained by Asami and Tiokura in the polymerization of styrene under the action of $SnCl_4$ and BF_3 etherate in liquid sulfur dioxide ([3]).

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