CHEMISTRY

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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MOLECULAR-WEIGHT DISTRIBUTION OF STEREOREGULAR POLYBUTADIENE DURING POLYMERIZATION UNDER THE INFLUENCE OF "COBALT" SYSTEMS

In recent years, a number of works have reported the possibility of synthesizing regularly structured cis-1,4-polybutadiene under the influence of cobalt catalysts soluble in a hydrocarbon medium ($^{1-4}$). The main components of the catalytic system are cobalt complex salts soluble in hydrocarbons and dialkylaluminum halides. As we established earlier (^{2}), the molecular weight of the butadiene polymers formed in this case is inversely dependent on the concentration of cobalt salts (C_c). In polymerization in solution at a temperature of +5°, according to the data of work (^{4}), this dependence is described by the equation $\bar{M} = k/C_c$; with increasing temperature a gradual transition to the dependence $M = k/C_c$ is observed.

Fig. 1. M.w.d. of polybutadienes obtained by polymerization in the presence of $CoCl_2 + Al(iso\text{-}C_4H_9)_2Cl$.
1 –conversion 20% ($M_0 = 245\,000$, $\overline{M}_n = 270\,000$, $\overline{M}_w = 320\,000$).
2 –conversion 97% ($M_0 = 90\,000$, $\overline{M}_n = 136\,000$, $\overline{M}_w = 265\,000$)

In the present work, changes in the molecular weight and molecular-weight distributions (m.w.d.) of polymers were studied as functions of the concentration of monomer in solution and of the extent of polymerization. The polymerization of butadiene was carried out in benzene solution (10 wt. %) under the action of a catalytic system formed by the interaction of diisobutylaluminum chloride with the cobalt chloride–ethyl alcohol complex, according to the procedure described previously.

The molecular-weight distributions of the polymers were calculated on the basis of sedimentation data in an ultracentrifuge. To increase the resolving power

Figure 2

Figure 2: Figure 2

of the ultracentrifuge, a 1:1 mixture of hexane and heptane was used as solvent; it proved to be close to a thermodynamically ideal solvent. Sedimentation experiments were carried out at a temperature of 20° and centrifugal fields of $\sim 180\,000\,g$. The m.w.d. was calculated by the method described in the literature (^{5}), on the basis of the dependence we obtained of the sedimentation constant at infinite dilution s_0 on molecular weight.

In studying the m.w.d. of samples of butadiene polymers obtained at different stages of the polymerization process, it was found that, with increasing degree of conversion, the maximum of the m.w.d. curve shifts toward lower molecular-weight values (Fig. 1). As follows from Fig. 1, at a degree of conversion of 20%, with a $CoCl_2$ concentration of 0.01% and Al(iso-C_4H_9)Cl 2% relative to monomer, at 30° the maximum of the polymer m.w.d. curve (M_0) lies in the region of 245,000. Calculated from the cur-

weight MWD, the weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights of this polymer proved to be, respectively, 320,000 and 270,000. At 97% conversion the value of M_0 of the polymer lies in the region of 90,000, and the weight fraction of fractions with molecular weight up to 100,000 increases noticeably. The average molecular weights of the polymer thereby decrease to $\overline{M}_w = 265\,000$ and $\overline{M}_n = 136\,000$. An analogous dependence of the MWD on the degree of conversion is observed in the polymerization of butadiene under the action of the catalytic system $CoBr_2 \cdot C_2H_5OH$—Al(iso-$C_4H_9)_2$Cl (Fig. 2).

From the data presented on the molecular weights of the polymers obtained it follows that, in the polymerization of butadiene on a cobalt complex catalyst, five or more polymer molecules are formed per molecule of $CoCl_2$ or $CoBr_2$, i.e., in the indicated process regeneration of catalytic centers takes place. In this connection, the concentration of $CoCl_2(CoBr_2)$ in the system remains practically unchanged with the depth of polymerization. At the same time, however, a considerable decrease in the monomer concentration occurs. Thus, the data obtained directly indicate that the decrease in molecular weight and the change in the character of the MWD of the polymer with the depth of polymerization that we have observed are due to the concomitant decrease in the concentration of monomer in the system. A dependence of the molecular weight of the polymer on the concentration of butadiene was also observed in work (^{4}).

Fig. 2. MWD of polybutadienes obtained by polymerization in the presence of $CoBr_2 +$ Al(iso-$C_4H_9)_2$Cl.
1 –conversion 30% ($M_0 = 155\,000$, $\overline{M}_n = 160\,000$, $\overline{M}_w = 202\,000$);
2 –conversion 100% ($M_0 = 71\,000$, $\overline{M}_n = 82\,000$, $\overline{M}_w = 162\,000$).

Fig. 3. Scheme of the process of butadiene polymerization on the complex catalyst $CoCl_2 +$ Al(iso-$C_4H_9)_2$Cl with portionwise addition of monomer and

Figure 3

Figure 3: Figure 3

Fig. 4. M.w.d. of polybutadienes obtained with portionwise introduction of monomer and solvent.

Figure 4: Fig. 4. M.w.d. of polybutadienes obtained with portionwise introduction of monomer and solvent.

solvent. The arrows indicate the moments of introduction of monomer and solvent.

The influence of the concentration of monomer and catalyst on the molecular weight and MWD of the polymers formed, as well as the fact of regeneration of catalytic complexes, was clearly manifested in experiments on the polymerization of butadiene with portionwise introduction of its solutions into the system. In the indicated experiments the polymerization of butadiene was carried out in benzene solution (10 wt.%) at a temperature of 30° under the action of the catalytic system $CoCl_2 \cdot C_2H_5OH + Al(iso\text{-}C_4H_9)_2Cl$. After 18 h, after reaching

at 100% monomer conversion, a new portion of butadiene and benzene was introduced, equal to that introduced at the start of the process (Fig. 3). The polymerization process was thereby resumed without introducing additional amounts of catalyst. The rate of the process decreased somewhat, which was apparently due to a decrease in the concentration of catalyst and monomer in the solution, and also to an increase in the viscosity of the latter. Sixty-six hours after 100% conversion of the second portion of monomer had been reached, a third portion of butadiene and benzene, equal to the initial one, was introduced; here again the polymerization process was resumed without introducing additional amounts of catalyst, and the polymerization of butadiene proceeded to 100% conversion.

Fig. 4. M.w.d. of polybutadienes obtained with portionwise introduction of monomer and solvent. 1 –1st portion, 2 –2nd and 3rd portions. ($M_v = 55\,000$, $\overline{M}_n = 68\,000$, $\overline{M}_w = 180\,000$)

The data presented in Fig. 3 not only confirm the fact of regeneration of the catalytic complex, but also indicate that this complex retains its activity for a long period of time. The polymers obtained at a 100% degree of polymerization of each portion of butadiene, as follows from Fig. 4, are characterized by practically identical m.w.d. This result is evidently connected with the fact that, upon portionwise introduction of the butadiene solution into the system, there occurs, on the one hand, a decrease in the concentration of $CoCl_2$ (approximately by a factor of 2 upon introduction of the second portion and by a factor of 3 upon introduction of the third), which should be accompanied by a shift of the m.w.d. curve into the region of high molecular-weight values. On the other hand, there is at the same time a corresponding decrease in the concentration of butadiene in the solution, which, as noted above, is accompanied by a shift of the m.w.d. into the region of low molecular weights. Under the conditions of the experiments, these two processes probably compensate one another, and the resulting m.w.d. of the polymers prove to be identical.

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