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Abstract

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FEATURES OF THE MECHANISM OF MOLECULAR-CHAIN TERMINATION DURING POLYMERIZATION UNDER THE ACTION OF COMPLEX CATALYSTS

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At present, in order to obtain polymers characterized by a highly regular structure of the molecular chains, complex catalysts of the Ziegler-catalyst type are widely used. In this connection, the elucidation of the mechanism of the individual stages of the polymerization process under the action of these catalysts becomes of fundamental importance. The present communication gives some results of a study of the mechanism of isoprene polymerization under the action of a complex catalyst formed by the interaction of Al $(iso\text{-}C_4H_9)_3$ and $TiCl_4$, obtained on the basis of data from sedimentation of polymers in an ultracentrifuge in combination with data on the kinetics of polymerization.

We have previously shown (^{1}) that, in the polymerization of isoprene under the action of the indicated catalyst, the growth of macromolecules occurs very rapidly, and the time interval from the moment of initiation of an active chain to its deactivation is measured in small fractions of a minute. As a result, a steady state is established in the system practically at once. However, the experimentally obtained molecular-weight distributions of polymers with the aid of the ultracentrifuge differ fundamentally from the equilibrium distributions corresponding to the kinetic schemes of polymerization known up to the present time. They are characterized by a comparatively small dispersion and, most importantly, are strongly shifted into the high-molecular-weight region; in the polymer, in most cases, macromolecules with molecular weights below 200–300 thousand are practically absent.

The features cited for the polymers we have studied can be interpreted only on the basis of new hypotheses, since no known mechanism leads to narrow molecular-weight distributions in the presence of chain-termination reactions. It is necessary to seek a termination mechanism that is highly sensitive to the molecular weight (length) of the chain, as a result of which chain rupture occurs only within a certain, sufficiently narrow interval of molecular weights. We believe that this mechanism is due to the heterogeneity of the polymerization reaction, i.e., to the fact that during its growth the polymer chain is attached by one end to the catalytic complex on the surface of the catalyst. Attachment of the end of the macromolecule to a plane imposes restrictions on the possible configurations of the polymer chain, since the half-space on the other side of the restricting plane becomes forbidden for its segments. Consequently, detachment of the macromolecule from the surface will be accompanied by an increase in configurational entropy by an amount ΔS, equal to the difference between the logarithms of the statistical sums for a chain far from the wall (in solution) and for a chain near the wall with one end fixed to it.

Using, for calculating the number of possible configurations of the polymer chain, the quasi-lattice method with coordination number γ for the segments, ···

located in the volume, and $\gamma/2$ for segments located on the surface, we determined that the "defect" of the configurational entropy (ΔS) increases with an increase in the number of kinetic segments in the polymer chain (z) according to the equation

$$\Delta S = k\sqrt{z} \tag{1}$$

(k is the Boltzmann constant).

To make the subsequent discussion more specific, we shall proceed from the model of growth of a polymer chain in heterogeneous catalytic polymerization that is at present the best substantiated. According to this model, the growing polymer chain has, at its active end, an alkyl- or haloalkylaluminum group. The latter forms with titanium halide on the catalyst surface a catalytic complex by means of a bridging ("half-valence") bond. This bond is characterized by an energy of 10-15 kcal/mole and is evidently the weakest link connecting the polymer molecule with the surface. Consequently, detachment of such a molecule from the catalyst surface most probably occurs precisely along this bond, i.e., is accompanied by dissociation of the catalytic complex. Natta and co-workers were the first to point out the possibility of reversible dissociation of catalytic complexes ([2]).

Let us consider separately the reactions of dissociation of the catalytic complex and of its restoration. The rate constant of a chemical reaction (K) is determined by the relation

$$K = \frac{kT}{h} e^{-\frac{\Delta U^{*} - T\Delta S^{*}}{kT}}, \tag{2}$$

where k is the Boltzmann constant, h is the Planck constant, ΔU^{*} is the activation energy, and ΔS^{*} is the activation entropy.

The activated state for a monomolecular dissociation reaction preserves the structure of the initial complex, i.e., the macromolecule, as in the initial state, is bound to the surface. Therefore the activation entropy in the case under consideration, as in other monomolecular reactions, is small, and $T\Delta S^{*} \ll \Delta U^{*}$. Consequently, the rate constant for detachment of polymer chains from the catalyst surface is $K_1 \simeq 10^2$—10^4 s^{-1}. Such a large value of K_1 indicates that the growth of the polymer chain must be interrupted repeatedly as a result of dissociation of the active center at the bridging bond. In this case aluminum remains at the end of the chain, and its growth can be resumed after restoration of the catalytic complex. The rate of the reverse reaction of restoration of the catalytic complex, when one of the reactants is a polymer molecule, is determined not by the activation energy, which in this case is small, but by the activation entropy, the value of which depends on the dimensions of the polymer chain. Indeed, in this reaction the activated state differs little in its structure from the final one, i.e., the transition to the activated state is associated with anchoring the end of the polymer chain on the surface. In this case, however, as follows from equation (1), the configurational entropy of the chain decreases by an amount $\Delta S = k\sqrt{z}$. The latter, for a sufficiently large value of z, constitutes the principal part of the activation entropy for the reaction of restoration of the catalytic complex.

It follows from the above that the probability of finding a macromolecule in solution (x) or attached to the surface ($1 - x$) is determined by the following relation:

$$\frac{x}{1-x} = e^{-\frac{\Delta U - T\Delta S}{kT}}, \tag{3}$$

where ΔU is the energy that must be expended to detach the polymer molecule from the catalyst surface.

On the basis of relations (1) and (3), we obtained the following equation for the molecular-weight distribution of the polymer:

$$\frac{dw}{dM} = \frac{\sqrt{\frac{M}{rM_0}}\, e^{-\frac{\Delta U}{kT}} + \sqrt{\frac{M}{rM_0}}}{2\left(1 + e^{-\frac{\Delta U}{kT}} + \sqrt{\frac{M}{rM_0}}\right)^2}, \tag{4}$$

where w is the weight fraction, r is the number of monomer units in the kinetic segment, and M_0 is the molecular weight of the monomer.

Fig. 1. Molecular-weight distributions of polyisoprenes.
1 –Al(iso-$C_4H_9)_3 : TiCl_4 = 1 : 1$. The catalyst was aged for 24 h. Polymerization temperature 0°.
2 –fresh catalyst Al(iso-$C_4H_9)_3 : TiCl_4 = 1 : 1$;
3 –Al(iso-$C_4H_9)_3 : TiCl_4 = 1 : 1 + 0.5$ Al(iso-$C_4H_9)_3$ (with monomer);
4 –Al(iso-$C_4H_9)_3 : TiCl_4 = 1 : 1 + 1$ Al(iso-$H_4H_9)_3$.
2–4 polymerization temperature 30°.

This distribution is characterized by a curve whose dispersion coefficient ($\delta M/M$) is determined by the equation

$$\frac{\delta M}{M} \simeq \frac{3kT}{\Delta U}. \tag{5}$$

Thus, the dispersion of the distribution curve is determined by the bonding energy of the growing polymer molecule with the catalyst surface. For $\Delta U \simeq$ 10–15 kcal/mol, the dispersion coefficient of the molecular-weight distribution is approximately equal to 0.1, i.e., very small. Consequently, the proposed mechanism of molecular-chain termination during polymerization under the action of heterogeneous complex catalysts implies the possibility of obtaining polymers with a very narrow molecular-weight distribution. Such a polymer was in fact obtained by us

Fig. 2. Kinetic curves of isoprene polymerization at 30°C.
1 –Al(iso-$C_4H_9)_3 : TiCl_4 = 1 : 1$;
2 –the same +0.5 Al(iso-$C_4H_9)_3$ (with monomer);
3 –Al(iso-$C_4H_9)_3 : TiCl_4 = 1.5 : 1$.

by polymerizing isoprene in pure monomer at low temperature (0°) under the action of a catalyst aged for 24 h, with the ratio of its components equal to 1 : 1. In Fig. 1, curve 1 gives the distribution curve of this polymer in the coordinates dw/ds (s is the sedimentation constant in octane at a polymer concentration of 2 mg/ml), which is characterized

with a dispersion coefficient equal to 0.1, which corresponds to a dispersion coefficient of the molecular-weight distribution curve of approximately 0.15.

Thus, complex catalysts are distinguished not only by stereospecificity, but also, under certain conditions, ensure the production of polymers with a high degree of homogeneity. The chain-termination mechanism set forth above is manifested, however, only in the case where the growth of the macromolecules is not interrupted earlier. One of the factors causing "premature" termination of molecular chains is the presence in the catalyst of free triisobutylaluminum (^{3}). We verified this fact in special experiments in which a catalyst prepared in advance (component ratio = 1 : 1) was introduced into a monomer containing dosed amounts of Al(iso-$C_4H_9)_3$. In this case, at the beginning of polymerization, while the excess Al(iso-$C_4H_9)_3$ remains in the free state, the rate of polymerization remains approximately the same as it would have been without the addition of the free organoaluminum compound (Fig. 2), but the molecular-weight distributions of the polymers shift sharply into the region of low molecular weights (Figs. 1, 3, 4). These facts indicate that the mechanism of chain termination under the action of the chemically unbound organoaluminum compound is similar to the mechanism of the transfer reaction, i.e., proceeds with regeneration of active centers. Evidently, for the same reason, during polymerization with a freshly prepared catalyst (at a component ratio = 1 : 1), which still contains some amount of free Al(iso-$C_4H_9)_3$, low-molecular-weight fractions are found in the polymer being formed; these are absent in polymerization with the same catalyst aged for 24 hours (Fig. 1, 1, 2).

The results presented make it possible to conclude that, in catalytic polymerization, termination of molecular chains by the transfer mechanism occurs only in the particular case where a free organoaluminum compound or other components capable of transfer reactions are present in the system. In the absence of the indicated components, termination of molecular chains occurs by the mechanism specific to heterogeneous polymerization, set forth above.

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References Cited

1. S. E. Bresler, M. I. Mosevitskii, I. Ya. Poddubnyi, N. N. Chesnokova, *ZhTF*, **28**, 2487 (1958).
2. G. Natta, J. Pasquon, *Atti Accad. Naz. Lincei. Rendi Sci. fis.*, **26**, No. 45, 617 (1959).
3. G. Natta, I. Pasquon, E. Giachetti, *Chim. et Ind.*, **40**, 97 (1958).

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