

**V. N. ZGONNIK,
Corresponding Member of
the Academy of Sciences
of the USSR B. A.
DOLGOPLOSK,**

V. A. KROPACHEV and N. I. NIKOLAEV

1962

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196201.82671>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Fig. 1. Dependence of the degree of conversion of butadiene on polymerization time at different temperatures: 1 -50° ; 2 -35° ; 3 -20° ; 4 -5° C

Figure 1: Fig. 1. Dependence of the degree of conversion of butadiene on polymerization time at different temperatures: 1 -50° ; 2 -35° ; 3 -20° ; 4 -5° C

Fig. 2. Dependence of the polymerization rate on the concentration of butadiene in solution

Figure 2: Fig. 2. Dependence of the polymerization rate on the concentration of butadiene in solution

Abstract

Full Text

CHEMISTRY

V. N. ZGONNIK, Corresponding Member of the Academy of Sciences of the USSR B. A. DOLGOPLOSK,
V. A. KROPACHEV and N. I. NIKOLAEV

SOME REGULARITIES OF THE PROCESS OF BUTADIENE POLYMERIZATION UNDER THE INFLUENCE OF "COBALT" CATALYTIC SYSTEMS

In a number of communications (¹⁻⁵), catalytic systems were described that contain cobalt compounds or their complexes and dialkylaluminum chlorides, which made it possible to obtain the most stereoregular polybutadiene with a high content of cis-1,4 units.

In the present article, some new data are reported on the regularities of the process of butadiene polymerization under the influence of a homogeneous catalytic system consisting of the pyridine complex of cobalt chloride and diisobutylaluminum chloride. The method of investigating the polymerization rate and determining the molecular weight of the polymer obtained did not differ from that described previously (⁴). Butadiene polymerization was carried out in benzene solution at temperatures of $5-50^{\circ}$, at a monomer concentration of 1.2 mole/l, CoCl_2Py_2 $2.1 \cdot 10^{-5}$ mole/l and $\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$ $1.5 \cdot 10^{-2}$ mole/l (polymer yield about 40%).

Fig. 1. Dependence of the degree of conversion of butadiene on polymerization time at different temperatures: 1 -50° ; 2 -35° ; 3 -20° ; 4 -5° C

Fig. 2. Dependence of the polymerization rate on the concentration of butadi-

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

ene in solution

Figure 1 presents data on the kinetics of polymerization at various temperatures. The polymerization process is characterized by a small induction period, which may be connected with the stage of formation and “maturation” of the catalytic complex or with the presence in the system of a certain amount of impurities inhibiting the polymerization.

Table 1

$T, ^\circ\text{C}$	$W \cdot 10^{-5}, \text{mole/cm}^3 \cdot \text{sec}$	$M_\eta \cdot 10^{-3}$
5	0.78	396
20	2.53	159
35	5.02	115
50	6.80	82

Table 1 gives the average values for the polymerization rate and the molecular weight of the polymer, obtained from 3-4 parallel experiments.

The total activation energy of the process, calculated from these data, is 8.2 kcal/mole. The influence of monomer concentration at constant catalyst concentration on the polymerization rate was studied at

20°: the concentration of CoCl_2Py_2 was $3.5 \cdot 10^{-5}$ mole/liter, $\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$ $1.5 \cdot 10^{-2}$ mole/liter; the monomer concentration was varied from 6 to 23 mole %. It follows from Fig. 2 that the rate of polymerization is directly proportional to the monomer concentration. Fig. 3 illustrates the dependence of the polymerization rate on the content of CoCl_2Py_2 for benzene solutions containing 15 mole % butadiene at 20°. The concentration of CoCl_2Py_2 was varied from $9 \cdot 10^{-6}$ to $7.6 \cdot 10^{-5}$ mole/liter. In the indicated interval the rate of polymerization is directly proportional to the concentration of CoCl_2Py_2 . The figures given below illustrate the rectilinear dependence of the molecular weight of the polymer on the monomer concentration:

Fig. 3. Dependence of the polymerization rate on catalyst concentration

Fig. 4. Molecular-weight distributions for samples of polybutadiene. **A** – polymerization temperature 20°. Concentration of CoCl_2Py_2 : 1 – $1.05 \cdot 10^{-5}$; 2 – $4.2 \cdot 10^{-5}$ mole/liter. **B** – polymerization temperature 2°. 1 – conversion 9%; 2 – conversion 15%; 3 – conversion 65%

Butadiene conc., mole %	6.0	11.5	17.8	23.4
$M_n \cdot 10^{-3}$	200	340	470	610

Assuming conditionally that each molecule of CoCl_2Py_2 participates in the formation of an active center and, consequently, also in the reactions of initiation and chain growth, one can calculate the final average molecular weight of the polymer under the condition that each act of chain termination is accompanied by the death of active centers. However, the results of the calculation, summarized in Table 2, show that a large number of polymer molecules are formed per initial molecule of CoCl_2Py_2 , whence it follows that the acts of chain termination are accompanied by regeneration of active centers.

We obtained a series of molecular-weight distributions for polybutadiene samples with conversion below 10%. From Fig. 4A it is seen that as the concentration of CoCl_2Py_2 in the solution decreases, the molecular weight of the polymer increases, while the width of the distribution decreases ($\overline{M}_w/\overline{M}_n$ changes from 1.05 to 1.5). Earlier, in work (4), we presented molecular-weight distributions for two samples of polybutadiene obtained at high conversion, and it was established that in this case the value of $\overline{M}_w/\overline{M}_n$ was close to 2. To correlate these distributions, we studied-

molecular-weight distributions of polybutadiene samples taken from the ampoules at different degrees of polymerization were recorded.

The molecular-weight distributions obtained as a function of the degree of polymerization are shown in Fig. 4 B. From the character of the distribu-

Table 2

CoCl_2Py_2 , $\text{mol} \cdot 10^{-6}$	C_4H_6 , $\text{mol} \cdot 10^{-3}$	$M_{\text{high}} \cdot 10^{-5}$	$\overline{M}_n \cdot 10^{-5}$	$M_{\text{high}}/\overline{M}_n^*$
1.05	18.1	935	60.2	15.5
4.20	18.1	234	38.0	6.2
14.70	6.0	22	4.7	5.7

* Number of polymer molecules formed per 1 molecule of CoCl_2Py_2 .

tions it may be concluded that, for the catalytic system $\text{CoCl}_2\text{Py}_2-\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$, the width of the molecular-weight distribution increases with the degree of polymerization, and at the same time the molecular weight of the polymer increases.

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

Received
7 V 1962

REFERENCES

1. G. J. Natta, Pol. Sci., 48, 150, 221 (1960).
2. B. A. Dolgoplosk, E. N. Kropacheva et al., DAN, 135, 847 (1960).
3. C. Longiave, R. Castelli, G. F. Croce, Chimica e Industria, 43, No. 6, 625 (1961).
4. V. N. Pronkin, B. A. Dolgoplosk et al., Vysokomolek. soed., 4, No. 7 (1962).
5. M. Gippin, Rubb. Age, 89, 802 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.