Chemistry

A. A. Arest-Yakubovich, Academician S. S. Medvedev

1964

SovietRxiv

Abstract

Full Text

Chemistry

A. A. Arest-Yakubovich, Academician S. S. Medvedev

ANIONIC POLYMERIZATION OF BUTADIENE IN TETRAHYDROFURAN

Up to the present time, the anionic polymerization of dienes in solvents with a high solvating ability with respect to the counterion has been studied rather little. Only the polymerization of butadiene and isoprene on lithium initiators has been investigated kinetically ([1,2]).

We have studied the kinetics of the polymerization of butadiene in THF under the action of complexes of alkali metals with diphenyl over a wide temperature range. In most cases the measurements were carried out by the dilatometric method. The kinetics of the fastest processes—with potassium and cesium initiators at –30° and above—were studied by determining the yield of polymer after a known time in a thermostated reactor with a rapidly acting stirrer. At –96° the solubility of the initiator decreases noticeably and it partially precipitates. Therefore, for initiation at –96° "living" prepolymers obtained as a result of a preliminary reaction of the initiator with a small amount of monomer were used. At other temperatures no delayed initiation was observed, and the polymerization rates on the prepolymer and on the initiator were equal.

Table 1

Rate constants of growth in the polymerization of butadiene in tetrahydrofuran, l/mol · sec

Temperature, °C	Counterion Na^+	Counterion K^+	Counterion Cs^+
+10	5.4	~ 70	~ 50
–30	1.8	17.0	7.3
–43	1.05	–	–
–56	0.60	3.1	1.6
–82	0.40	–	–
–96	0.29	0.16	0.05
A, l/mol · sec	$1.6 \cdot 10^4$	$3.1 \cdot 10^6$	$5 \cdot 10^6$
E, kcal/mol	4.4*	5.9	6.5

* Above –56°.

As shown by spectrophotometric ([3]) and kinetic data, "living" polybutadiene at room temperature gradually isomerizes into an inactive form, analogous to

Fig. 1. Temperature dependence of the growth rate

Figure 1: Fig. 1. Temperature dependence of the growth rate

Fig. 2. Temperature dependence of the microstructure of polybutadiene

Figure 2: Fig. 2. Temperature dependence of the microstructure of polybutadiene

polystyrene (^{4,5}). On a prepolymer obtained at room temperature (holding time before the beginning of polymerization 10–15 min) from sodium- and potassium diphenyl, butadiene polymerizes at $-96°$ twice as slowly as on a prepolymer obtained at $-60°$, or with direct initiation.

In polybutadiene the isomerization proceeds faster than in polystyrene, since holding the latter for 30–40 min at room temperature has little effect on the active properties of carbanions with sodium and potassium counterions (^{5}). This is probably connected with the fact that the butadiene carbanion is less stable than the styryl carbanion.

The change in the reaction rate with the depth of conversion is well described by an equation of first order with respect to the monomer. At $-96°$ the polymerization rate is proportional to the concentration of the initiator when it is varied from $2 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ mol/l. Thus, phenomena of association of active centers do not play an essential role for sodium and potassium counterions in THF. Owing to the absence of chain-termination and chain-transfer processes, the kinetic data obtained make it possible directly to determine the rate constants (Table 1) and Arrhenius parameters (Fig. 1) for the chain-growth reaction.

The data obtained indicate a strong dependence of the growth rate on the nature of the counterion, in contrast to the polymerization of styrene, where with Li, Na, K, and Cs initiators at 2° practically identical rates were obtained (^{5}). Comparison with data obtained for polymerization on lithium compounds (^{1,2}) shows that at temperatures above $-60°$ the growth rate in the series Li $<$ Na $<$ K increases on passing from one metal to another by approximately an order of magnitude.

Fig. 1. Temperature dependence of the growth rate

Fig. 2. Temperature dependence of the microstructure of polybutadiene

A certain decrease in the rate on passing from K to Cs (Table 1) is possibly, to some extent, connected with the sharply increased rate, for Cs, of isomerization of the active centers (^{5}). However, since in the present work the experiments were carried out not on prepolymers but with direct initiation, the degree of deactivation cannot be high, as is confirmed by the closeness of the molecular weights to those calculated by the formula $\overline{M}_n = 2M/C$. In any case, it is beyond doubt that the transition from K to Cs does not cause a further increase in the reactivity of the active centers. The activation energies for Li (6.1–6.3

kcal/mole (^{1,2})), K, and Cs are close; for Na the activation energy is somewhat lower.

In the low-temperature region a sharp break is observed in the Arrhenius-dependence line for sodium-initiated polymerization (Fig. 1), which below −56° gives $k_p = 16e^{-1400/RT}$. With potassium, cesium, and, apparently, lithium, such a break is not observed, and polymerization down to −96° proceeds with a constant temperature coefficient. The slight temperature dependence for sodium polymerization leads to the fact that at −96° its rate noticeably exceeds the rate of polymerization with potassium and cesium counterions. In this region the activity series of the alkali metals has the form Na > K > Cs Li.

The nature of the counterion affects not only the kinetics of polymerization but also the microstructure of polybutadiene (Table 2). In contrast to kinetic measurements, which for diene monomers give averaged values over the different growth processes, the study of the polymer microstructure makes it possible to judge the relative weight of the principal growth directions:

$$\frac{\text{percent of 1,4 structure}}{\text{percent of 1,2 structure}} = \frac{k_{1,4}}{k_{1,2}} = \frac{A_{1,4}}{A_{1,2}} e^{-(E_{1,4}-E_{1,2})/RT}.$$

The temperature dependence of the microstructure (Fig. 2) shows that 1,2-addition proceeds with a lower activation energy than 1,4. Therefore

At low temperatures all the polymers contain about 90% of 1,2-units. The structure of the polybutadiene obtained in the presence of lithium and sodium depends little on temperature. On the other hand, potassium and cesium are characterized by a rather strong temperature dependence of the microstructure, corresponding to $\Delta E \simeq 2$ kcal/mol. As a result, the polymers obtained with potassium and cesium diphenyl at temperatures above 0° have a rather high (up to 40–45%) content of 1,4-units.

The dependence of the polymerization rate and the structure of polybutadiene on the nature of the counterion is evidently associated with the differing ability of the cations of the alkali metals to form solvates with the solvent (THF) and to interact with the carbanion. The magnitude of the electrostatic interaction of the carbanion with the counterion, which lowers the rate of chain growth, at the same degree of solvation decreases with increasing cation radius (^{6}). The activity series Li < Na < K obtained in the present and earlier works (^{6,7}) agrees with these ideas.

Table 2

Microstructure of polybutadiene as a function of the conditions of preparation

Temp., °C	Structure*	Li^+	Na^+	K^+	Cs^+
+40	1	84.0	–	56.6	–
+40	2	8.4	–	36.5	–
+40	3	7.6	–	6.9	–
+10	1	85.6	79.3	63.5	60.6
+10	2	7.2	15.5	30.4	31.4
+10	3	7.2	5.2	6.1	8.0
−30	1	–	82.9	76.4	72.7
−30	2	–	15.6	20.7	27.3
−30	3	–	1.5	2.9	0
−56	1	91.0	88.0	83.5	82.9
−56	2	9.0	12.0	14.8	17.1
−56	3	0	0	1.7	0
−96	1	–	92.7	88.3	89.0
−96	2	–	7.3	11.7	10.9
−96	3	–	0	0	0
$A_{1,4}/A_{1,2}$		0.8	1.5	16	27
$E_{1,4} - E_{1,2}$, cal		900	1100	1900	2100

* 1 –1,2; 2 –trans-1,4; 3 –cis-1,4.

On the other hand, as was pointed out earlier (6), it is necessary to take into account the possibility of formation of solvates of different structure, whose composition may depend not only on the nature of the counterion (decrease in the degree of solvation in the series Li > Na > K > Cs), but also on temperature (3). In particular, the anomalous course of the temperature dependence for sodium-initiated polymerization (see Fig. 1) may be connected with the appearance at low temperatures of highly active higher solvates. Then the observed temperature coefficient will reflect not only the activation energy of chain growth, but also the heat effect of the transition from lower solvates to higher ones.

According to preliminary data, changing to a solvent with an even greater solvating ability than THF, dimethoxyethane, causes a significant (up to 10-fold) increase in the rate of sodium-initiated polymerization of butadiene.

The authors consider it their pleasant duty to express gratitude to A. R. Gantmakher for interest in the work and discussion of the results, and also to N. V. Desyatova for determining the microstructure of polybutadiene by IR spectroscopy.

Physico-Chemical Institute
named after L. Ya. Karpov

Received
13 VII 1964

CITED LITERATURE

1. Yu. L. Spirin, D. K. Polyakov et al., DAN, **139**, 899 (1961).
2. M. Morton, E. E. Bostick et al., J. Polymer Sci., **A1**, 1735 (1963).
3. D. K. Polyakov, Yu. L. Spirin et al., DAN, **150**, 1051 (1963).
4. M. Levy, M. Szwarc et al., Polymer, **1**, 515 (1960).
5. A. I. Nepomnyashchii, Kh. S. Bagdasaryan, Kinetics and Catalysis, **4**, 198 (1963).
6. R. V. Basova, A. R. Gantmakher, S. S. Medvedev, DAN, **158**, No. 4 (1964).
7. R. V. Basova, A. A. Arest-Yakubovich et al., DAN, **149**, 1067 (1963).

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

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