Diene Polymerizations with Lanthanide Coordination Catalysts.
III. Kinetic Stereocontrol of Polybutadiene Microstructure

Z. M. SABIROV*, N. KH. MINCHENKOVA and YU. B. MONAKOV

Institute of Chemistry, Bashkirian Research Centre, USSR Academy of Sciences, Ural Department, Prospekt Oktyabrya 71, Ufa, Su-450054 (U.S.S.R.)

Abstract

Butadiene polymerization has been investigated with the Nd–Al catalytic system with a low monomer concentration. By theoretically analyzing the data, an equation has been derived to connect the ratio of formation rates of 1,4-*cis*- and 1,4-*trans*-units to the current monomer concentration, that being in good conformity with the experiment. On the basis of the results obtained, the mechanism of kinetic stereocontrol of polybutadiene microstructure has been determined in the system under consideration.

Introduction

With dienes polymerized on *cis*-regulating catalytic systems, the changes in relative content of 1,4-*cis*- and 1,4-*trans*-units depending on the polymerization conditions applied are often explained within the mechanism of kinetic stereocontrol of the microstructure, which consists of the chain propagation reaction first forming an anti-structure of the end chain which is further isomerized into a thermodynamically more stable *syn*-structure [1]. The relative contents of 1,4-*cis*- and 1,4-*trans*-units depend here on the ratio of isomerization and propagation rates. The above concept was first used to explain an appreciable increase in the content of 1,4-*trans*-units in polydienes (with low initial monomer concentrations <0.4 mol/l) in polymerizations effected by catalytic systems based on d-elements [2]. The authors of refs. 3 and 4 reported that one should take into account the possible *anti-syn*-isomerization of the end units in the growing chain to interpret the formation mechanism of polydiene microstructure on lanthanide catalytic systems. However, there are no specific accounts in the literature to cover this problem.

The paper presented has been aimed at verification of the kinetic stereocontrol of microstructures
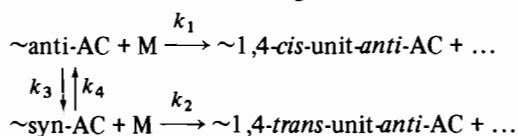
formed in butadiene polymerization effected by the Nd–Al catalytic system.

Experimental

The catalytic complex was prepared as in ref. 3 with Nd:Al = 1:40. Polymerization was conducted in toluene at 80 °C. Polymer microstructures were identified by the IR spectral method.

Results and Discussion

The dependence of the polymerization rate on the monomer concentration has been analyzed to show that the reaction is first order with respect to the monomer (Fig. 1). Accordingly, the chain propagation reaction with an account for *anti-syn*-isomerization of active centres (AC) can follow the structural–kinetic scheme given below.

$$\sim\text{anti-AC} + \text{M} \xrightarrow{k_1} \sim 1,4\text{-}cis\text{-unit-}anti\text{-AC} + \ldots$$

$$k_3 \updownarrow k_4$$

$$\sim\text{syn-AC} + \text{M} \xrightarrow{k_2} \sim 1,4\text{-}trans\text{-unit-}anti\text{-AC} + \ldots$$

where k_1 and k_2 are rate constants of monomer addition to *anti*-AC and *syn*-AC, respectively; $k_3(k_4)$ are rate constants of *anti-syn*- (*syn-anti*-)-isomeriza-

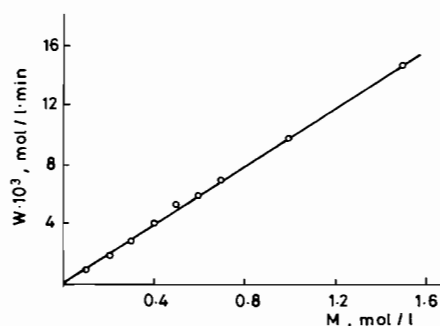Fig. 1. The dependence of butadiene polymerization rate on the initial monomer concentration at 80 °C.

tion; ~anti-AC and ~syn-AC stand for anti- and syn-isomeric forms of AC; M = butadiene. The above scheme does not specify the formation of 1,2-units for their contents is ⩽1%. According to the scheme, it follows

$$-\frac{d[M]}{dt} = k_1[anti\text{-}AC][M] + k_2[syn\text{-}AC][M] \quad (1)$$

$$\frac{d[anti\text{-}AC]}{dt} = -k_3[anti\text{-}AC] + k_4[syn\text{-}AC] \quad (2)$$
$$+ k_2[syn\text{-}AC][M]$$

where [anti-AC] ([syn-AC]) and [M] are the concentrations of anti- (syn-)-forms of AC and of the monomer, respectively.

The formation rates of 1,4-cis-(V_{cis})- and 1,4-trans-(V_{trans})-units can be derived as

$$V_{cis} = k_1[anti\text{-}AC][M] \quad (3)$$

$$V_{trans} = k_2[syn\text{-}AC][M] \quad (4)$$

and

$$[anti\text{-}AC] + [syn\text{-}AC] = C_a^\circ \quad (5)$$

where C_a° is the total concentration of AC.

Equation (2) considered in quasi-stationary approximation proves the concentrations of AC isomeric forms connected by the following relation

$$\frac{[syn\text{-}AC]}{[anti\text{-}AC]} = \frac{k_3}{k_4 + k_2[M]} \quad (6)$$

Using eqns. (3), (4) and (6), the following relationship should be valid for the anti-syn-isomerization of AC

$$\frac{V_{cis}}{V_{trans}} = \frac{k_1 k_4}{k_2 k_3} + \frac{k_1}{k_3}[M] \quad (7)$$

which connects the ratio of formation rates of 1,4-cis- and 1,4-trans-units in the polymer to the current monomer concentration at a given instant $M(t)$.

The peculiar feature of eqn. (7) lies in that it does not involve an AC concentration which is rather difficult to estimate. It becomes thus possible to compare experimental data obtained with various AC concentrations. Equation (7) enables also the estimation of the ratio of rate constants for elementary stages of the chain propagation reaction in each case to facilitate thus the further definition of their absolute values.

To check eqn. (7), the dependence of polybutadiene microstructure of the initial monomer concentration ([M] = 0.1–0.6 mol/l) and conversion has been investigated. By the data thus obtained, V_{cis} and V_{trans} values have been calculated (with difference expressions). For instance, V_{cis} value at an instant $t = t_1 + \Delta t/2$ (where t_1 = origin of reading for Δt interval) has been estimated as

$$V_{cis} = \Delta[1,4\text{-}cis]/\Delta t$$

where $\Delta[1,4\text{-}cis]$ is the change in the concentration of 1,4-cis-units for the time interval Δt. The content of 1,2-units is always ⩽1% and this value has been added to that of the concentration of 1,4-trans-units. The resulting dependence of V_{cis}/V_{trans} on the current monomer concentration $M(t)$ is outlined in Fig. 2 to be well-described by a straight-line dependence as in eqn. (7). The correlation coefficient $\rho = 0.98$. By simple analysis it can be found that $k_1/k_3 = 10.1 \pm 0.5$ l/mol and $k_1 k_4/k_2 k_3 = 0.9 \pm 0.1$. From $k_4 \neq 0$, it follows that the reaction of AC anti-syn-isomerization is an equilibrium one.

To estimate the constant values for elementary stages, one should analyze eqn. (1) for the rate of chain propagation reaction V_p, which can be conveniently written down as below accounting for eqns. (5) and (6).

$$V_p = K_{eff}C_a^\circ[M]; K_{eff} = \frac{\alpha + 1 + \beta[M]}{\alpha + k_1/k_2 + \beta[M]} \times k_1 \quad (8)$$

where $\alpha = k_1 k_4/k_2 k_3$ and $\beta = k_1/k_3$, k_{eff} is the effective constant of the propagation reaction rate.

What should the k_1/k_2 values be for the realization of the observed first-order propagation reaction with respect to the monomer? It should be noted that with [M] = 0.1–0.6 mol/l, $\alpha = 0.9$ and $\beta = 10$ l/mol, neither addendum in the numerator of eqn. (8) can be neglected. If $k_1/k_2 \ll \alpha + \beta[M]$, $k_{eff} = k_1(1 + \alpha + \beta[M])/(\alpha + \beta[M])$ and the k_{eff} value should be approximately 1.5-fold decreased with the monomer concentration changed from 0.1 to 0.6 mol/l. However, it does not conform to the experiment. If $k_1/k_2 \gg \alpha + \beta[M]$

$$V_p = (1 + \alpha)k_2 C_a^\circ[M] + \beta k_2 C_a^\circ[M]^2 \quad (9)$$

Accounting for $\beta/(1 + \alpha) = 5$, it is clear that the contribution of the quadratic member in eqn. (9) must not be neglected as compared to the linear one. The latter assertion is also at variance with the experiment. Therefore, there remains to assume $k_1 = k_2$. Here $V_p = k_1 C_a^\circ[M]$ and the first-order reaction is realized, that being experimentally confirmed. As
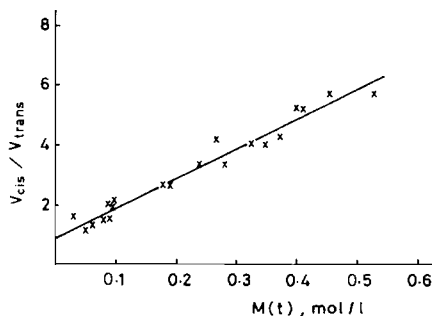

Fig. 2. The dependence of V_{cis}/V_{trans} value on the current monomer concentration $M(t)$ at 80 °C.

far as the equality of k_1 to k_2, one should note the following. If *anti*- and *syn*-structrues of AC differ by nothing but the isomeric end unit of the growing chain, it is difficult to anticipate that they would appreciably differ by their reactivity, particularly when there always occurs the formation of end 1,4-units. From this point of view, the $k_1 = k_2$ condition becomes physically clear.

One should also consider that the equality of k_1 to k_2 enables the estimation of isomerization constants $K = k_4/k_3 = 0.9$. The value of constant K close to unity means that thermodynamically isomeric structures of AC are practically equivalent with a slight preference for *syn*-structures.

Conclusions

Therefore, the studies reported here give evidence to the occurrence of kinetic stereocontrol of the polymer microstructure, i.e. of the content of 1,4-*cis*- and 1,4-*trans*-units, in butadiene polymerization effected by an Nd—Al catalytic system. Here, the ratio of formation rates (propagation) of 1,4-*cis*- and 1,4-*trans*-units depends linearly on the current monomer concentration. By the analysis of the data obtained, the reaction of AC *anti-syn*-isomerization has been assumed to be in equilibrium and the AC isomeric structures have been found equal by both their thermodynamic stability and reactivity.

References

1 B. A. Dolgoplosk and E. I. Tinyakova, *Metalloorganitcheskyi kataliz v protsessakh polimerizatsii*, Nauka, Moscow, 1982.
2 B. A. Dolgoplosk, K. L. Makovetskyi, L. I. Red'kina, T. V. Soboleva, E. I. Tinyakova and V. A. Yakovleva, *Dokl. Akad. Nauk SSSR, 205* (1972) 387.
3 Yu. B. Monakov, N. G. Marina, I. G. Savel'eva, L. E. Zhiber, N. V. Duvakina and S. R. Rafikov, *Dokl. Akad. Nauk SSSR, 278* (1984) 1182.
4 J. Ouyang, F. Wang and J. Yang, in G. Xu and J. Xiao (eds.), *New Front. Rare Earth Sci. Appl., Proc. Int. Conf. Rare Earth Dev. Appl.*, Vol. 1, Sci. Press, Beijing, 1985, pp. 606–613.