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Kinetic Manifestation of Active Centre Structure in Diene Polymerization Assisted by Lanthanide Catalytic Systems

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The reactivity of active polymerization centres has been found to depend on the nature of the diene in the presence of which a lanthanide catalytic system had been prepared; this effect was assumed to be due to the existence of two reactive bonds, Ln–C and Ln–C–Al, in the active centre.

Among many problems created by the reaction mechanism of lanthanide catalytic systems, the greatest importance is attached to that of the nature of the active centre responsible for the polymer chain growth. As is the case with conventional Ziegler–Natta catalysts, lanthanide systems are peculiar because of the bridging bonds between metal atoms, those bridges being built by either chlorine atoms or alkyl or hydride groups. One would therefore expect that the terminal unit of the growing polymer chain either joins a transition metal atom according to the monometallic model of active centres, or forms a bridge bond simultaneously with a transition metal atom and an aluminium atom according to the bimetallic model of active centres, as reported in some publications.[1–4] However, it is quite possible that the actual active centre involves both types of bonds that differ appreciably by their reactivity. Hence, it is natural to assume certain kinetic manifestations of the active centre due to their specific structure. This problem is analysed in this communication.

Two sets of catalytic systems were studied in butadiene polymerization conducted in toluene at 25 °C. Each catalyst was prepared in the presence of a small amount of diene. The first set consisted of the following systems: $NdCl_3 \cdot 3L$-penta-1,3-diene-AlR_3 **1**, $NdCl_3 \cdot 3L$-butadiene-AlR_3 **2**, $TbCl_3 \cdot 3L$-penta-1,3-diene-AlR_3 **3** and $TbCl_3 \cdot 3L$-butadiene-AlR_3 **4**, where L is tributylphosphate and $AlR_3 = Al(i\text{-}C_4H_9)_3$. The catalytic systems were prepared by mixing toluene solutions of $LnCl_3 \cdot 3L$, a diene and AlR_3 at their mole ratios [Al]/[Nd(Tb)] = 30 and [diene]/[Nd(Tb)] = 2 for *ca.* 120 min at room temperature. The catalytic systems of the second set were prepared by adding new portions of butadiene (B) to the systems **1** and **3** and new portions of pentadiene (P) to the systems **2** and **4** at [diene]/[Nd(Tb)] = 10. The delay time was from 12–1440 min at room temperature. Thus, the second set consisted of the following catalytic systems: **5** = **1** + B, **6** = **3** + B, **7** = **2** + P and **8** = **4** + P.

Upon butadiene polymerization with the system **1** or **3** prepared in the presence of pentadiene, the effective constant of propagation rate K_{eff}, as found from $\ln(M_t/M) = -K_{eff} C_a t$ (M_t and M are the current and starting butadiene concentrations, respectively, C_a is the concentration of active centres and t is the polymerization time), is much higher than that with the systems **2** or **4** obtained with butadiene addition (K_{eff} = 330, 220, 630 and 240 dm^3 mol^{-1} min^{-1} for **1**, **2**, **3** and **4**, respectively.

Under butadiene polymerization effected by any of the second-set catalysts, it was found that the longer the delay

Table 1 Dependence of K_{eff} on the delay time of the catalytic systems (toluene, 25 °C, butadiene polymerization).

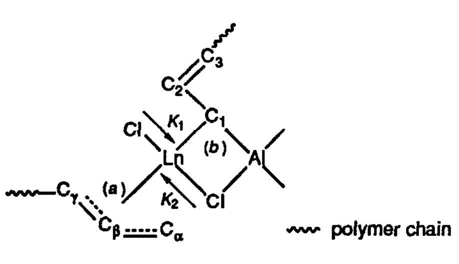
Delay time/min	K_{eff}/dm^3 mol^{-1} min^{-1} System **5**	System **7**	System **6**	System **8**
a	330	220	630	240
12	290	240	560	280
30	230		480	310
42		250		
72			340	340
90		260	280	430
120	230		280	
150				490
180		280	280	
240	220			520
300		300	240	
360	220			620
1440	220	300	240	630

[a] Values of K_{eff} for the starting catalytic systems **1–4**.

time for the systems **5** and **6**, the lower the reactivity of the active centre and the values of K_{eff} tended to reach those of the systems **2** and **4**, respectively (Table 1). Quite the reverse, the higher the delay time for the systems **7** and **8**, the higher the reactivity of the active centre and the values of K_{eff} reached those usual for the systems **1** and **3**, respectively (Table 1). It should be noted that neither addition of butadiene to **2** and **4** nor addition of pentadiene to **1** and **3** resulted in any changes in the reactivity of the active centres. As far as the polybutadiene microstructure is concerned, the content of 1,4-*cis*, 1,4-*trans*- or 1,2-units was found to change by as little as 0.5% in some of the experiments.

One may suppose that the above-stated variations of the active centre reactivity are none other than kinetic manifesttions of the specific features of the active centre in the lanthanide catalytic systems.

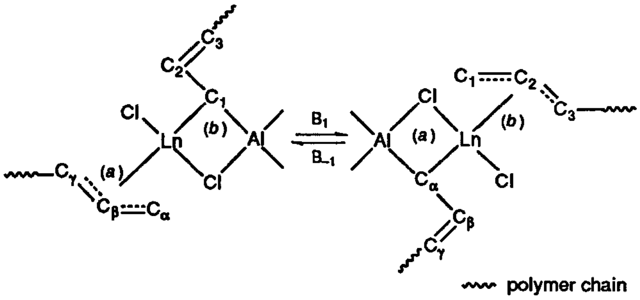
Within the bimetallic model of the active centre, it is quite possible that the active centre in the systems has two types of metal-carbon bonds simultaneously, which may be responsible for the reaction of monomer insertion into the polymer chain: a π-allylic bond (*a*) and a bridge Ln–C–Al (*b*), these being strongly different in their reactivity, *i.e.* $K_1 \neq K_2$:



It is not known as yet which of the two bonds shows higher reactivity. One cannot find reliable arguments in favour of $K_1 \gg K_2$ or $K_1 \ll K_2$. Thus, one may assume (for example) that the polymer chain grows mainly by a σ-bridging bond (*b*), *i.e.*, $K_1 \gg K_2$. This means that the active centre obtained in the presence of pentadiene or butadiene (the active centre has different σ-bridging and π-allylic ligands during the initial stage of polymerization) would differ only by the structure of their π-allylic ligands (*a*) as the polymerization proceeds because insertion of butadiene molecules into the σ-bridging bonds of the active centre abolishes the differences in their primary structure. Therefore, it is due to the different structures of the π-allylic ligands that the reactivity of the active centre varies during the initial stage of butadiene polymerization catalysed by the systems **1–4**.

In this case, it is natural to assume that the experimental variations in active centre reactivity, which depend on the delay time of the catalytic systems **5–8** (Table 1) are affected by substitution of the π-allylic ligands for a new one. This substitution may be realized in two possible ways.

The first implies slow growth of the polymer chain directly by the π-allylic bond with propagation rate constant K_2. The π-allylic structure is usually supposed to turn into an allylic one before the coordinated molecule is put into the polymer chain. The second way implies the occurrence of an equilibrium reaction:



Due to the fact that the organoaluminium compound is migrating, the π-allylic bond is transformed into the bridge and *vice-versa*.

The active centre structure suggested in this work is peculiar in that both bonds (π-allylic and σ-bridging) are built by the same Ln atom, hence minor changes in the electron structure of one of the bonds (as for butadiene substituted for pentadiene) would affect the second bond with respect to its electron structure (ionicity, atom charge values, *etc.*) and naturally its reactivity.

Taking into account the possibility of more complicated structures of the catalytic Nd–Al complex the π-allylic and σ-bridging bonds might be located on different metal centres and remote from each other. In this case, it would be difficult to rationalize the effect of the structure of one of the bonds on the reactivity of the other.

It would be important to note also that the structure of the π-allylic or σ-bridging ligand affects the ability of the active centre to coordinate with solvent molecules, free molecules of $\mathrm{AlR_3}$ or complexes of $\mathrm{AlR_3}$ with electron-donor molecules in the system.[5]

Therefore, the initial reactivity of the active centres in lanthanide catalytic systems depends on the structure of the diene used to prepare the catalytic system. As judged by variations in active centre reactivity during the polymerization process, the lanthanide active centre may have two types of metal-carbon bonds that are appreciably different in reactivity.

References

1 M. C. Throcmorton, *Kautsch. Gummi Kunstst.*, 1969, **22**, 293.
2 A. Mazzezi, *Makromol. Chem.*, 1981, **182**, Suppl. 4, 61.
3 C. Shan, E. Lin, J. Ouyang, Y. Fan and G. Yang, *Makromol. Chem.*, 1987, **188**, 629.
4 N. G. Marina, Yu. B. Monakov, Z. M. Sabirov and G. A. Tolstikov, *Vysokomol. Soedin*, 1990, **33**, 467 [*Polym. Sci. USSR (Engl. Transl)*, 1990, **33**, 387].
5 Z. G. Shamaeva, N. G. Marina, Yu. B. Monakov and S. R. Rafikov, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1982, 846 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, 743).

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