Diene Polymerizations with Lanthanide Coordination Catalysts.
II. The Effects of Catalytic System Component Types and Polymerization Conditions on Molecular Characteristics of 1,4-*cis*-Polybutadienes

V. G. KOZLOV, N. G. MARINA, I. G. SAVEL'EVA, YU. B. MONAKOV, YU. I. MURINOV and G. A. TOLSTIKOV

Institute of Chemistry, Bashkirian Research Centre, USSR Acad. Sci. Ural Department, Ufa 450054, U.S.S.R.

(Received May 18, 1988)

Abstract

Molecular inhomogeneity has been investigated for 1,4-*cis*-polybutadienes obtained with a lanthanide-containing catalytic system; some kinetic parameters have been estimated for polymerizations. Gel-permeation chromatography was chosen as the main method to find out the average molecular weights (MW) and molecular weight distributions (MWD). The catalyst composition has been shown to effect MW and MWD. The molecular characteristics are determined by both the catalyst composition and the polymerization conditions (reagent concentration, temperature). The broad MWD is considered a peculiarity of butadienes prepared with lanthanide-containing catalysts. The data obtained lead to the assumption that the distribution of the polymerization centres by reactivity is responsible for the broad MWD of the polybutadienes formed.

Introduction

Catalytic systems based on lanthanides have roused the interest of research chemists because of the effective production of polydienes with a high content of 1,4-*cis*-units. The literature data available are mainly concerned with studies into the effects of synthesis conditions and of types and compositions of catalytic systems on the process kinetics and polydiene microstructures [1, 2]. Much less attention has been paid to investigations of molecular weight characteristics of polydienes.

This report covers our studies into the effects of lanthanides, halides and organic ligand types in the catalytic systems employed, and of the polymerization conditions on the molecular weights and molecular weight distributions of 1,4-*cis*-polybutadienes (PB). Also some kinetic parameters have been calculated for the polymerization process.

Experimental

The average molecular weights ($\bar{M}$) and molecular weight distributions (MWD) of the polybutadienes were determined by gel permeation chromatography on a KHZH-1302 chromatograph equipped with Waters Styragel columns with $3 \times 10^2 – 5 \times 10^6$ Å pore size at 25 °C using chloroform as solvent. The system was calibrated by the Waters polystyrene standards according to the universal Benoit plot [3, 4]. The kinetic constants (k_p = rate propagation constant; k_t^m, k_t^{Al} = rate constants of chain transfer on monomer and triisobutylaluminium, respectively) were calculated in accordance with the reported equations [5]. The active centre concentrations (C_a) were estimated by the method of dosed introduction of a non-radioactive inhibitor [6]; freshly distilled cyclopentadiene was used here.

Results and Discussion

1,4-*cis*-Polybutadienes prepared with the lanthanide catalytic system contained neither a gel fraction nor branched macromolecules throughout the whole range of molecular weights observed. As a consequence, the values for average molecular weights and MWD estimated by gel permeation chromatography give an actual picture of the polymerization kinetics. The kinetic constants calculated from the above values are represented in Table I. The k_p values obtained from the kinetic data are shown to agree well to those established with inhibition.

The effect of the lanthanide on the PB molecular characteristics has been investigated with catalytic systems containing complexes of Ce, Nd and Gd halides. With the catalysts based on neodymium and gadolinium chlorides, polymers with similar molecular weights and MWD values (Fig. 1) are produced, while the PB obtained with the Ce catalyst reveals a much lower molecular weight and

TABLE I. Kinetic Parameters of Butadiene Polymerization with $LnHal_3 \cdot 3L-Al(i\text{-}C_4H_9)_3$ [a]

$LnHal_3 \cdot 3L$	Kinetic method						Inhibition	
	k_p	C_a	k_t^m $(\times 10^2)$	k_t^m/k_p $(\times 10^4)$	K_o^{Al}	k_t^{Al}/k_p $(\times 10^2)$	k_p	C_a
$NdCl_3 \cdot 3TBP$	140	6.7	1.0	0.7	9.5	7.1	140	7.0
$NdCl_3 \cdot 3TBP$[b]	470	7.0						
$GdCl_3 \cdot 3TBP$	140	7.0	1.3	0.9	7.0	5.0	130	6.5
$CeCl_3 \cdot 3TBP$	30	5.5	2.7	9.0	1.7	6.0	40	7.0
$NdBr_3 \cdot 3TBP$	140	7.0	1.2	0.9	7.0	5.0	150	7.4
$NdCl_3 \cdot 3DÁSO$	70	10.0	2.0	3.0	2.4	3.5		

[a] $T_{polym} = 25\ °C$, toluene = solvent, k_p and $k_t = 1/\text{mol min}$, $C_a = (\text{mol/mol Ln}) \times 10^2$. [b] Heptane = solvent.
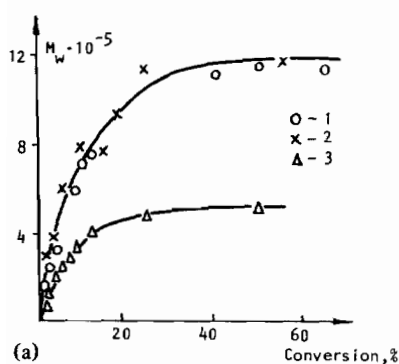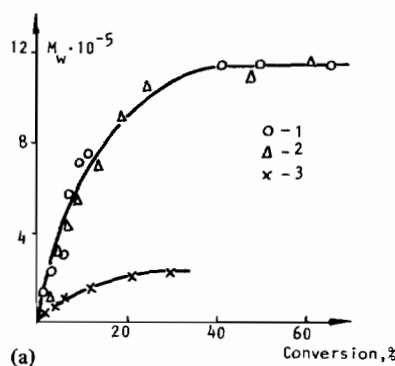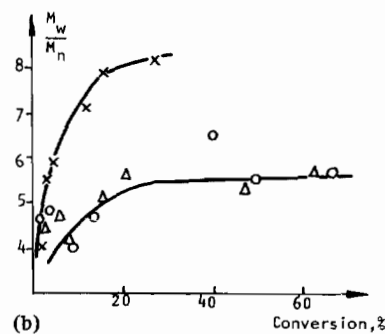

(a)
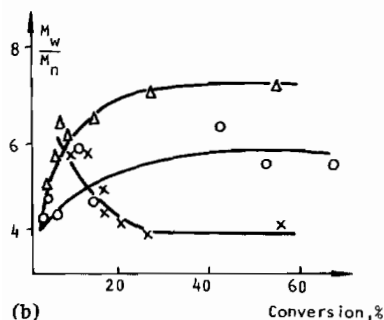
(b)

Fig. 1. The dependence of PB molecular weight (a) and poly-dispersity (b) on the conversion with the system $LnCl_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$, where Ln = Nd(1), Gd(2), Ce(3). Conditions: solvent = toluene, $C_M = 1.32$, $C_{Ln} = 1 \times 10^{-3}$ mol/l, Al/Ln = 20, $T_{polym} = 25\ °C$.

(a)

(b)

Fig. 2. The dependence of PB molecular weight (a) and poly-dispersivity (b) on the conversion with the system $NdHal_3 \cdot 3L-Al(i\text{-}C_4H_9)_3$, where Hal = Cl(1, 3), Br(2); L = TBP(1, 2), DASO(3). Conditions: see Fig. 1.

broader MWD (Fig. 1) under otherwise equal conditions. The kinetic constants have been found to be rather similar to each other in polymerizations with Nd and Gd catalysts (Table I). The employment of Ce catalysts results in a pronounced decrease in k_p and in enhancement of the chain-transfer processes; thus, this has been considered to be the reason for the lower values of $\bar{M}$ for polybutadienes produced with cerium catalytic systems.

The type of halogen involved in the catalytic systems exerts no observable influence on the PB molecular weight (Fig. 2). With catalysts based on complexes of $NdCl_3$ and $NdBr_3$, a plot of $\bar{M}$ against the conversion rate (U) results in the usual curve due to the similar values of the kinetic constants of chain propagation and chain transfer for these catalysts (Table I). However, the increasing polydispersity with the increasing conversion and the higher rate of the latter are inherent to PB synthesized with a chlorine-containing catalyst. Still, the M_w/M_n value decreases in the initial polymerization step for the polymer prepared with a bromine-containing catalytic system. The narrowing of the MWD with the conversion growth becomes distinctive only for catalysts containing $NdBr_3$.

The PB molecular characteristics are considerably effected by the organic ligand (L) in the complexes of LnHal$_3$·3L. With catalysts containing tributyl-phosphate (TBP) as L changed for the systems with diamylsulfoxide (DASO), the PB molecular weight decreases and the polydispersity increases (Fig. 2). The said change of molecular weight is caused by the polymerization kinetic parameters; *i.e.* the DASO-based systems are characterized by both the lower k_p values and the increasing role of the chain-transfer-to-monomer reactions (Table I).

The polymerization conditions also exert a considerable influence on the PB molecular characteristics. As seen in Figs. 1 and 2, irrespective of the catalyst composition the PB molecular weight increases at the initial step, while $\bar{M}$ discontinues its growth when the conversion has reached 20–30%. Further polymerization results in no observable changes of the polymer molecular characteristics, which suggests the existence of chain-transfer reactions and a stable number of active centres in the system. The polybutadiene MWD reveals its tendency to broadening when the conversion increases to 30%, any further increase being practically absent (Figs. 1, 2). The system containing neodymium bromide is an exception, as the polydispersity of the PB decreases with increasing conversion.

An increased concentration of the lanthanide component of the catalyst (with the Al/Ln ratio being constant) results in a decreased $\bar{M}$ for the poly-butadiene (Table II). The chain-transfer constant calculated from the data of Table II is found to be similar to the k_t^{Al} value for the related system. Besides, the varied content of the lanthanide component with the constant Al(i-C$_4$H$_9$)$_3$ concentration leads to no observable changes in the PB molecular characteristics (Table II). Therefore, LnHal$_3$·3L cannot be considered as a chain-transfer agent and the main part in the transfer process of a propagating chain is taken by triisobutylaluminium, according to Fig. 3. For this reason, an increased Al(i-C$_4$H$_9$)$_3$ concentration results in a considerable decrease in the PB molecular weight for the systems studied (Fig. 3). It should be noted that changes in the content of the organoaluminium compound are also followed by essential changes in the polymer MWD.

The butadiene concentration may serve as a control parameter of the molecular characteristics (Fig. 4). The $\bar{M}$ growth with increasing monomer content is caused by the accelerated rate of the macromolecular chain propagation ($W = k_p C_M C_a$), while the total rate of chain-transfer reactions reveals no considerable changes due to the low k_t^M value inherent to all the systems under study (Table I).

An increase in the polymerization temperature results apparently in an increase in the importance of the chain-transfer processes which would explain the pronounced lowering of the PB molecular weights (Fig. 5). Still, one should not turn the temperature effect into changes in the ratio of chain-propagation and chain-transfer rates. As seen in Fig. 5, the poly-butadiene MWD is also substantially effected by a change in the polymerization temperature.

TABLE II. The Dependence of PB Molecular Characteristics on the Lanthanide Component Concentration (C_{Ln}) in the Catalyst LnHal$_3$·3L–Al(i-C$_4$H$_9$)$_3$ (at 25 °C with toluene as solvent)
1. NdCl$_3$·3TBP, C_M = 1.76, C_{Al} = 3.0 × 10^{-2} mol/l;
2. GdCl$_3$·3TBP, C_M = 1.80, C_{Al} = 3.0 × 10^{-2} mol/l;
3. CeCl$_3$·3TBP, C_M = 2.03, C_{Al} = 5.0 × 10^{-2} mol/l;
4. NdBr$_3$·3TBP, C_M = 1.70, C_{Al} = 4.0 × 10^{-2} mol/l;
5. NdCl$_3$·3DASO, C_M = 1.96, C_{Al} = 5.0 × 10^{-2} mol/l;
6. NdCl$_3$·3TBP, C_M = 1.76, Al/Ln = 20

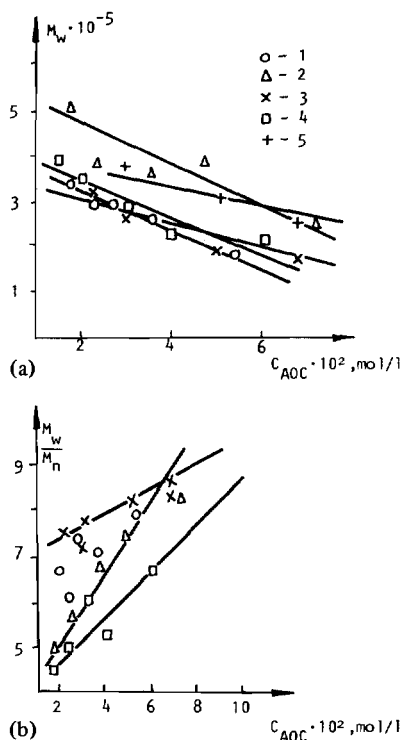| Catalytic system	C_{Ln} × 10^3 (mol/l)	M_w (×10^{-3})	M_n (×10^{-3})	M_w/M_n	Catalytic system	C_{Ln} × 10^3 (mol/l)	M_w (×10^{-3})	M_n (×10^{-3})	M_w/M_n
1	0.5	210	32	6.6	4	0.7	247	38	6.5
	0.8	212	37	5.7		1.0	237	45	5.3
	1.1	208	32	6.5		1.5	230	38	6.1
	1.5	226	36	6.1		1.8	233	37	6.3
2	0.8	384	56	6.8	5	0.8	264	30	8.8
	1.2	396	53	7.5		1.1	234	26	9.0
	1.5	373	52	7.2		1.5	258	30	8.6
	1.8	317	52	6.2		2.0	263	34	7.7
						2.5	218	25	8.7
3	1.0	197	22	9.0	6	0.5	570	96	5.9
	1.5	214	23	9.3		0.7	524	80	6.5
	1.7	162	21	7.7		0.9	367	55	6.7
	2.0	169	20	8.5		1.2	275	37	7.4
	2.5	189	21	9.0					

Fig. 3. The dependence of PB molecular weight (a) and polydispersity (b) on the Al(i-C$_4$H$_9$)$_3$ concentration with the system LnHal$_3$·3L–Al(i-C$_4$H$_9$)$_3$, where Ln = Nd(1, 4, 5), Gd(2), Ce(3); Hal = Cl(1–3, 5), Br(4); L = TBP(1–4), DASO (5). Conditions; solvent = toluene, C_M = 1.76(1), 1.85(2), 2.03(3), 1.90(4), 1.96(5) mol/l; $C_{Ln} \times 10^3$ = 0.9(1, 2, 4), 1.5(3, 5) mol/l; T_{polym} = 25 °C.

With the polymerizations carried out in solvents of different types, e.g. toluene and heptane, the PB molecular characteristics remain unchanged. However, the solvent exerts much influence over the value of the chain-propagation rate constant (Table 1). The k_p value is lower in toluene than that in heptane under otherwise equal conditions. Therefore, the k_t/k_p ratio is not affected noticeably by a change in solvent.

As follows from the regularities described above, the values of the average molecular weights and the order of their variations are determined by the polymerization kinetic parameters.

Among the peculiar properties of PB obtained with the lanthanide systems, the most important is the broad MWD which is also conditioned by the polymerization conditions and by the composition of the catalyst. The data obtained thus suggest that the active centres may involve an organic ligand and the solvent, because their individual chemical properties determine the k_p value. As follows from the data reporting that butadiene polymerization with lanthanide systems is of first-order in the monomer and catalyst [7] and from the above information
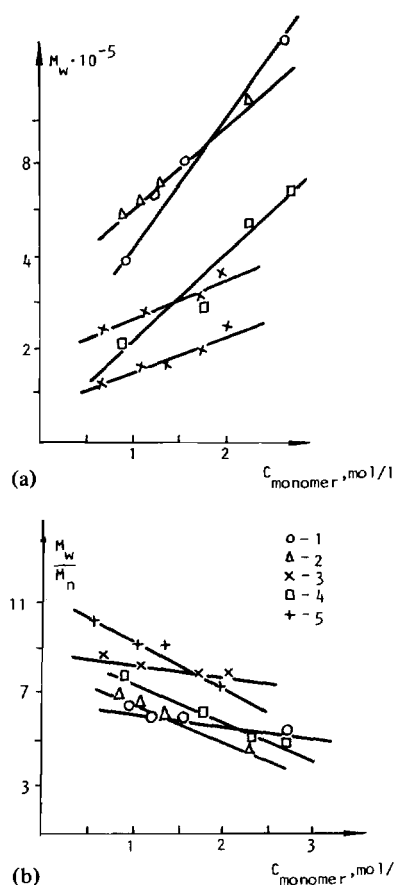

Fig. 4. The dependence of PB molecular weight (a) and polydispersity (b) on the butadiene concentration with the system LnHal$_3$·3L–Al(i-C$_4$H$_9$)$_3$, where Ln = Nd(1, 4, 5), Gd(2), Ce(3); Hal = Cl(1–3, 5), Br(4); L = TBP(1–4), DASO(5). Conditions: solvent = toluene, $C_{Ln} \times 10^3$ = 1.0(1, 2), 1.2(4), 1.5(3, 5) mol/l; Al/Ln = 20; T_{polym} = 25 °C.
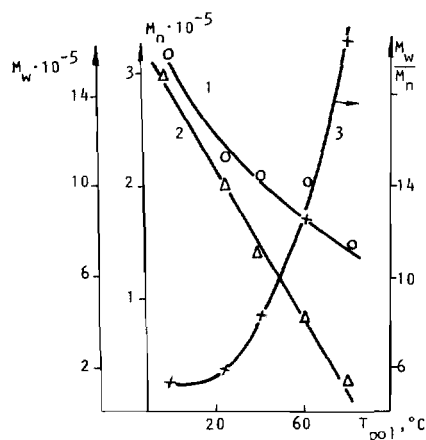

Fig. 5. The dependence of PB molecular weight and polydispersity on the polymerization temperature with the system NdCl$_3$·3TBP–Al(i-C$_4$H$_9$)$_3$; M_w(1), M_n(2), M_w/M_n(3).

for MWD, the polymerizations with the catalysts considered above probably involve several different active centres or, in other words, the distribution is affected by the reactivity of the polymerization centres.

The occurrence of different types of active centres may be caused, for instance, by the high coordination number of the 4f-elements. In addition to monomer and halogen, there can exist an organic ligand, solvent and AlR_3 in the Ln coordination sphere. One should take into account the possible involvement of different alkylated varieties of lanthanide halides in the process.

The above arguments suggest the assumption that the changes in composition of the lanthanide component of the catalytic system and in the polymerization conditions lead to different ligand environments for the lanthanide; *i.e.* to a changed distribution according to the reactivity of the active centres which thus results in the changed MWD of the polybutadienes.

Therefore, our report proves the catalyst composition (lanthanide, halide, organic ligand) and the polymerization conditions (monomer and $Al(i-C_4H_9)_3$ concentrations and temperature of the process) determine the molecular characteristics of 1,4-*cis*-polybutadienes. With changes in the said parameters polybutadiene samples with M_w from 1×10^5 to 1.5×10^6 and of $M_w/M_n = 4$–20 have been prepared.

References

1 Ouyang Jun, Wang Fosong and Jang Jihua, *New Front. Rare Earth Sci. Appl. Proc. Int. Conf. Rare Earth Der. Appl.*, *1*, 606 (1985).
2 N. G. Marina, Yu. B. Monakov, S. R. Rafikov and Kh. K. Gadeleva, *Vysokomol. Soedin.*, *Ser. A, 26*, 1123 (1984).
3 H. Benoit, Z. Crubisic and P. Rempp, *J. Polym. Sci.*, *5(B)*, 753 (1967).
4 V. G. Kozlov, V. P. Grigor'eva, A. A. Berg, Yu. B. Monakov, V. P. Budtov and S. R. Rafikov, *Prom. Sintet. Kautchuka*, *1*, 9 (1983).
5 N. M. Tchirkov, P. E. Matkovski, F. S. D'yatchkovsky, 'Polimerizatsiya na Kompleksnykh Metalloorganitcheskikh Katalizatorakh', Khimiya, Moscow, 1976, p. 415.
6 V. A. Zakharov, G. D. Bukatov, Yu. I. Ermakov and E. A. Demin, *Dokl. Acad. Nauk SSSR, 207*, 857 (1972).
7 Yu. B. Monakov, N. G. Marina, I. G. Savel'eva, L. E. Zhiber, V. G. Kozlov and S. R. Rafikov, *Dokl. Acad. Nauk SSSR, 265*, 1431 (1982).