

THE BIMODAL MOLECULAR WEIGHT DISTRIBUTION OF *cis*-POLYBUTADIENE POLYMERIZED WITH LANTHANIDE COMPLEX CATALYSTS

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ABSTRACT

The variation of the molecular weight and molecular weight distribution of *cis*-polybutadiene in the course of polymerization catalyzed by lanthanide complex composed of triisobutyl aluminium or diisobutyl aluminium hydride was investigated by osmometry, viscometry and size exclusion chromatography. By analyzing the experimental data, the reasons of the appearance of bimodal molecular weight distribution were elucidated and the possible mechanisms of polymerization were discussed.

The *cis*-polybutadiene polymerized with lanthanide complex catalysts usually possess a very broad molecular weight distribution^[1,2]. It was shown by the results of investigations on polymerization process that the lanthanide catalytical system has some features of living polymerization^[3,4]. The typical living polymers have very narrow molecular weight distribution just on the contrary to the case of polybutadiene polymerized with lanthanide catalyst. The complex catalysts of this polymerization system usually consist of lanthanide compounds, halides and alkyl aluminium. The average molecular weight and molecular weight distribution of the produced polymer changes with the variation of the composition of alkyl aluminium and sometimes bimodal distributions may appear^[5]. The occurrence of bimodal distribution definitely indicates that there are at least two kinds of mechanisms presented simultaneously in the polymerization process. The reasons for these complicated behaviours have not been elucidated yet. The alkyl aluminium usually used is triisobutyl aluminium (i-Bu)₃Al or diisobutyl aluminium hydride (i-Bu)₂AlH, but generally a mixture of these two compounds was used as a matter of fact. Recently, a kinetic study of butadiene polymerization using purified triisobutyl aluminium and diisobutyl aluminium hydride separately as one of the components of the complex catalyst was carried out. The products of this study were characterized by osmometry, viscometry and size exclusion chromatography in the present work. From the experimental results of the variation of the molecular weight and molecular weight distribution of the product with the conversion of the monomer, the reason of the occurrence of the bimodal distribution is elucidated and hence some valuable informations about the polymerization mechanism are obtained.

VARIATION OF MW AND MWD WITH CONVERSION

For the various *cis*-polybutadiene samples obtained in the course of polymerization with

different reaction time and conversion, their intrinsic viscosity in toluene was determined by capillary viscometer and their number average molecular weights were determined by membrane osmometer, the results obtained are listed in Table 1. The molecular weight distribution of these samples were also characterized by means of size exclusion chromatography. The mean elution volume $\bar{V}$, total variance σ_T^2 , intrinsic viscosity, number and weight average molecular weights and the inhomogeneity index D calculated from the experimental chromatogram $F(V)$ are also listed in Table 1.

Table 1 The molecular weight and SEC data of *cis*-polybutadiene samples

Alkyl	Time (min.)	Conversion x	$[\eta]$ (dl/g)	$\langle M \rangle_n \cdot 10^{-4}$ Osm.Pres.	SEC				
					$\bar{V}$	σ_T^2	$[\eta]$	$\langle M \rangle_n \cdot 10^{-4}$	D
Al(<i>i</i> -Bu) ₂ H	10	0.049	3.73	8.71	32.21	8.93	3.66	11.04	3.65
	20	0.084	3.17	5.55	32.64	9.96	3.39	8.38	4.48
	30	0.110	3.00	5.09	33.55	11.34	2.80	4.87	6.17
	40	0.187	2.60	3.67	33.79	11.97	2.71	4.29	6.87
	50	0.235	2.4	2.45	34.32	11.57	2.29	3.55	6.46
	60	0.349	1.87	2.55	35.03	10.23	1.78	2.94	5.44
Al(<i>i</i> -Bu) ₃	10	0.133	4.57	17.09	31.59	7.85	4.21	16.47	2.92
	20	0.216	5.24	21.65	31.05	7.56	4.80	21.26	2.66
	30	0.305	5.41	21.80	30.95	7.31	4.90	22.87	2.53
	40	0.375	5.60	22.37	30.43	7.50	5.65	26.89	2.58
	50	0.452	5.66	33.16	30.47	6.92	5.53	29.48	2.29

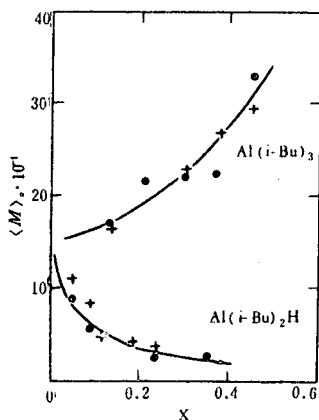


Fig. 1 The variation of the number average molecular weight of polybutadiene with conversion of monomer

+ SEC; ○ ● Osmometry

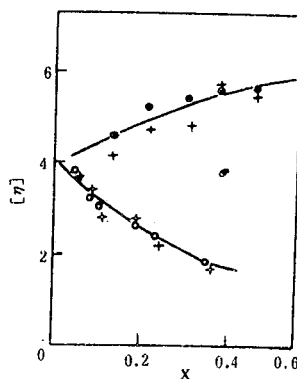


Fig. 2 The variation of intrinsic viscosity of polybutadiene with conversion of monomer

● Al(*i*-Bu)₃; ○ Al(*i*-Bu)₂H; Capillary viscometry; + SEC

The alkyl aluminium component of the lanthanide complex catalyst with unlike structure plays different role in the process of polymerization. The experimental data listed in Table 1 indicates that the behavior of triisobutyl aluminium and diisobutyl aluminium hydride are quite different. The following three experimental facts are especially spectacular.

First, the directions of the change of average molecular weight of the polymer produced with the conversion of monomer are completely different. The variation of the number average mole-

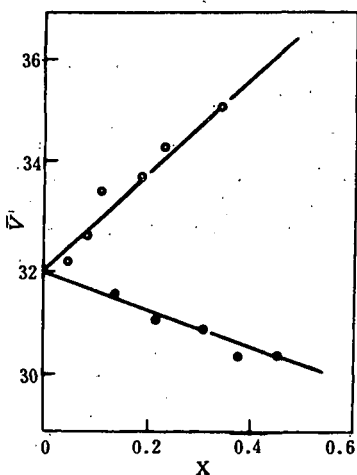


Fig. 3 The variation of mean elution volume of polybutadiene with conversion of monomer

● $\text{Al}(\text{i-Bu})_3$; ○ $\text{Al}(\text{i-Bu})_2\text{H}$

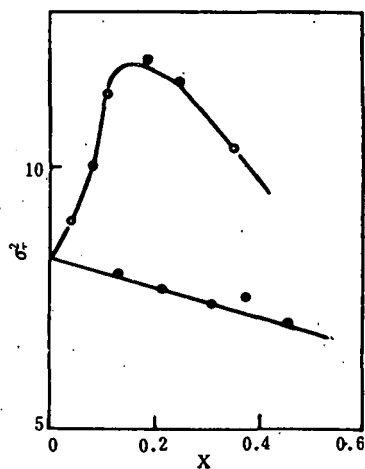


Fig. 4 The variation of total variance of SEC chromatogram of polybutadiene with conversion of monomer

● $\text{Al}(\text{i-Bu})_3$; ○ $\text{Al}(\text{i-Bu})_2\text{H}$

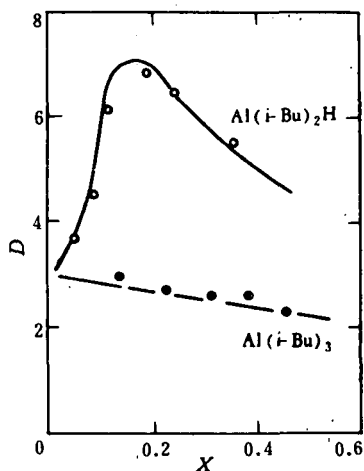


Fig. 5 The variation of inhomogeneity index of polybutadiene with conversion of monomer

● $\text{Al}(\text{i-Bu})_3$; ○ $\text{Al}(\text{i-Bu})_2\text{H}$

cular weight, intrinsic viscosity and mean elution volume of SEC chromatogram of the polymer with the conversion of monomer X as shown respectively in Fig. 1 to Fig. 3 all reflect the same rule, that is the average molecular weight of polybutadiene produced decreases with increasing conversion as diisobutyl aluminium hydride was used to compose the complex catalyst and on the contrary in the case of triisobutyl aluminium the average molecular weight of the product increases with increasing conversion of monomer.

Secondly, the variation of molecular weight distribution with conversion also follows different rules. The width of MWD can be directly characterized by the total variance of the experimental chromatogram. The variation of total variance and inhomogeneity index with conversion are shown in Fig. 4 and Fig. 5 respectively. As diisobutyl aluminium hydride is used the inhomogeneity index first increases and then decreases after passing through a maximum with increasing conversion of monomer. As triisobutyl aluminium is used the width of MWD of the polymer produced decreases monotonically with increasing conversion of monomer.

Thirdly, it can be seen from Fig. 1 to Fig. 5 that the number average molecular weight, intrinsic viscosity, mean elution volume, total variance and inhomogeneity index of the *cis*-polybutadiene polymerized with lanthanide catalysts composed of these two kinds alkylaluminium all have the same extrapolated value as the conversion of the monomer approaches to zero. It indicates that the initiation and propagation mechanisms are similar for both cases and other different reactions may be involved therein.

FORMATION OF BIMODAL MWD

When butadiene is polymerized with lanthanide complex catalyst composed of diisobutyl aluminium hydride or triisobutyl aluminium respectively, the molecular weight of the polymer produced in the former case decreases with increasing time or conversion, on the contrary it increases for the latter case. That is to say the product obtained at high conversion is a low molecular weight polymer for the former and vice versa for the latter. This difference in principle reflects the nonidentity of the polymerization mechanisms for the two cases and also explains why the MWD of lanthanide butadiene rubber is broad and the occurrence of bimodal distribution. Since the alkyl aluminium used for composing the catalyst actually is a mixture of alkyl aluminium and its hydride, the different mechanisms may play the role simultaneously in the course of polymerization and lead to the appearance of broad MWD or bimodal distribution.

Assuming for each polymerization mechanism a particular group of polymer is produced independently and the amounts of the produced polymer are proportional to the amount of the component in the mixture of alkyl aluminium and its hydride, then the molecular weight distribution of the produced polymer may be represented by the experimental SEC chromatogram $F(V)$ and could be written as

$$F(V) = w_1 F_1(V) + (1 - w_1) F_2(V),$$

in which w_1 is the weight fraction of diisobutyl aluminium hydride in the mixture, $F_1(V)$ and $F_2(V)$ are the normalized distribution of the polymer prepared with complex catalyst composed of pure diisobutyl aluminium hydride and triisobutyl aluminium respectively. Assuming $F_1(V)$ and $F_2(V)$ are Gaussian distribution which may be represented as

$$F_i(V) = [1/\sigma_{T,i}(2\pi)^{1/2}] \text{Exp} \{ -(1/2\sigma_{T,i}^2)(V - \bar{V}_i)^2 \}, \quad i = 1, 2$$

and using the interpolated or extrapolated values of mean $\bar{V}$ and variance σ_V^2 of the experimental distribution listed in Table 1 at the same conversion for the polymer produced with two kinds of alkyl aluminium to calculate the distribution $F(V)$ of *cis*-butadiene rubber at various conversions polymerized with lanthanide complex catalyst composed of 1:1 diisobutyl aluminium hydride and triisobutyl aluminium mixture, the calculated distributions are shown in Fig. 6. It can be seen that the bimodal distribution should progressively appear with increasing time and conversion of monomer. The variation of the calculated distribution of *cis*-butadiene rubber at higher conversion with composition of alkyl aluminium mixture is shown in Fig 7. These calculated results are in accord with the experimentally determined molecular weight distributions of butadiene-isoprene copolymer polymerized with lanthanide complex catalysts composed of alkyl aluminium mixed with its hydride^[6].

From the above numerical analysis it is shown that if the lanthanide complex catalyst is composed of a mixture of alkyl aluminium and its hydride, a bimodal molecular weight distribution should appear for the produced polymer at high conversion. It is believed that this situation is the consequence on that the excess of alkyl aluminium and its hydride over the complex required plays different role in the course of polymerization.

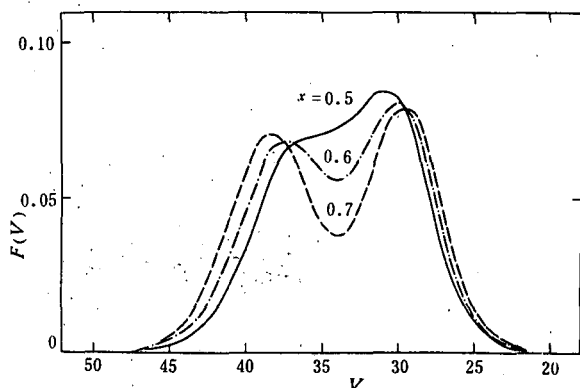


Fig. 6 The calculated molecular weight distribution of polybutadiene polymerized by a complex catalyst composed of a 1:1 mixture of triisobutyl aluminium and diisobutyl aluminium hydride at different conversion of monomer

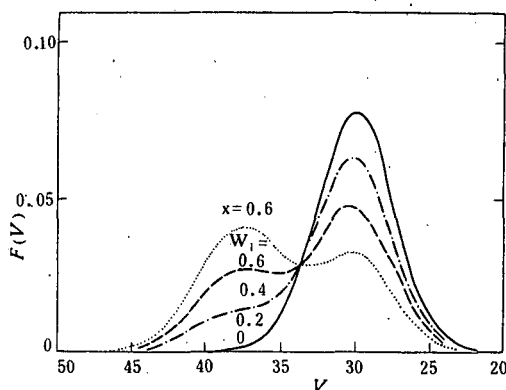
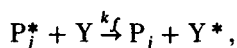
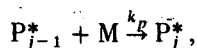


Fig. 7 The calculated molecular weight distribution or polybutadiene at $x = 0.60$ as a function of w_1

MECHANISM OF POLYMERIZATION

A possible source of the difference in the polymerization process of butadiene with unlike alkyl aluminium composing the lanthanide complex catalyst is due to the excess of the alkyl aluminium in the system behaves like a chain transfer agent or a molecular weight modifier and their chain transfer constants are different. Let Y denotes the chain transfer agent or modifier, P_j^* denotes the catalyst and propagating active center, M denotes monomer, then in the absence of termination reaction the polymerization process may be represented simply as



in which k_p and k_f are rate constants of propagation and chain transfer reaction respectively. From the results of the mathematical analysis of the kinetics of this process^[7], the relationship between number average degree of polymerization $\langle P \rangle_n$ of the polymer produced and the conversion of monomer x should be

$$\langle P \rangle_n = x[M]_0/[Y]_0[1 - (1 - x)^{c_f}]$$

in which $c_f = k_f/k_p$ is the chain transfer coefficient, $[M]_0$, $[Y]_0$ are the initial concentration of M and Y respectively. Following this relationship, the extrapolated number average degree of polymerization as $x \rightarrow 0$ is

$$\langle P \rangle_{n,0} = \lim_{x \rightarrow 0} \langle P \rangle_n = [M]_0/c_f[Y]_0$$

therefore the ratio $\langle P \rangle_n / \langle P \rangle_{n,0}$ should be

$$\langle P \rangle_n / \langle P \rangle_{n,0} = xc_f/[1 - (1 - x)^{c_f}].$$

According to this model, the absolute value or ratio of number average degree of polymerization may be either increase or decrease with increasing conversion of monomer depending upon whether the value of c_f is larger or smaller than one. Taking the extrapolated value of $\langle M \rangle_{n,0} = 15 \times 10^4$ as $x \rightarrow 0$ from Fig. 1, the dependency of $\langle M \rangle_n / \langle M \rangle_{n,0}$ on the conversion of monomer is shown in Fig. 8, in which the theoretical calculated lines with various c_f values are also drawn. As it is seen from the figure that when diisobutyl aluminium hydride is used as a component of the catalyst, the rate of decrease of the number average molecular weight of the polymer with increasing conversion is much more faster than the rate predicted by the model. On the other hand in the case of using triisobutyl aluminium although the change of the molecular weight ratio is more or less in accord with that predicted by the model for $c_f = 3 - 4$, but the fact that the absolute values of molecular weight of *cis*-butadiene rubber for which $c_f = 3 - 4$ are much more larger than that of the polymer prepared with diisobutyl aluminium hydride for which $c_f < 1$ could not be explained properly. Since these contradictions exist, it may be deduced that the difference of the role played by alkyl aluminium and its hydride in the polymerization of butadiene could not be simply explained by the difference in magnitude of chain transfer constant.

As lanthanide complex catalyst is used to polymerize dienes, some characteristic features of living polymerization appear, but the polymer has a broad molecular weight distribution which is contrary to the typical living polymers. Another possible explanation is that the formation of the catalytic active center is a slow process. For such a polymerization process without termination, the

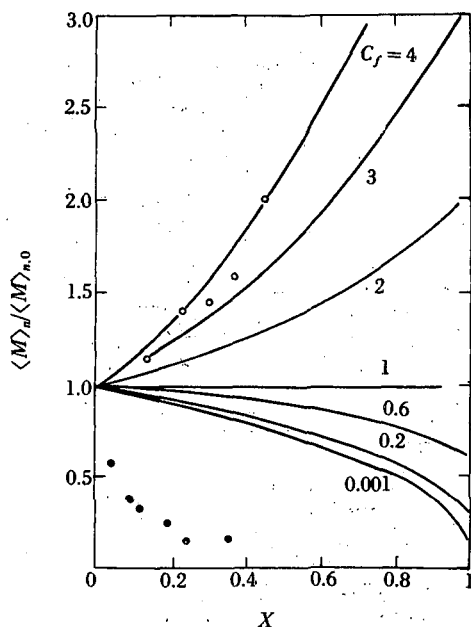


Fig. 8 The dependency of $\langle M \rangle_n / \langle M \rangle_{n,0}$ on the conversion of monomer

○ $\text{Al}(\text{i-Bu})_3$; ● $\text{Al}(\text{i-Bu})_2\text{H}$

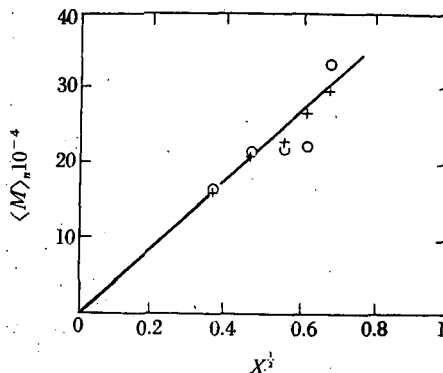


Fig. 9 The plot of $\langle M \rangle_n$ against $x^{1/2}$ for polybutadiene polymerized with $\text{Al}(\text{i-Bu})_3$ containing lanthanide complex catalyst.

○ Osmometry; + SEC

relation between the number average degree of polymerization of the product and the conversion of monomer may be expressed as^[7]

$$\langle P \rangle_n = (k_p / 2k_i)^{1/2} ([M]_0 x / [C])^{1/2}$$

in which k_i is the rate constant of initiation and $[C]$ is the concentration of catalyst. In Fig. 9 the number average molecular weight of *cis*-butadiene rubber polymerized with triisobutyl aluminium containing lanthanide catalyst is plotted against the square root of the conversion of monomer. It can be seen that the experimental points are located near a line passing through the origin as the model predicted. The decrease of the inhomogeneity index with increasing conversion is also in accord with the prediction of the model. By these facts it may be judged that the slow initiation model is in accord with the reality to a great extent. But this model cannot explain the principal feature about the polymerization of butadiene with diisobutyl aluminium hydride containing lanthanide catalyst, that is the molecular weight decreases with increasing conversion. This fact cannot be explained satisfactorily by chain transfer or termination of the active chain too, since a proper judgement requires that both the variation of molecular weight and molecular weight distribution are in accord with the prediction of model. A possible cause for the decrease of molecular weight is that more active centers are formed continuously or the polymer is degraded during the course of polymerization. Nevertheless, more theoretical and experimental investigations are required to decide whether this conjecture is true or not.

EXPERIMENTAL

The *cis*-polybutadiene sample used in the present work were polymerized with neodymium naphthenate-diisobutylchloroaluminium-alkyl aluminium complex catalyst at 50°C. The alkyl aluminium used was diisobutyl aluminium hydride and triisobutyl aluminium with 96.4% and 96.8% purity respectively.

The number average molecular weights of the samples were determined in toluene at 37°C by a Knauer membrane osmometer. The viscosity of the toluene solution of the sample was determined by a capillary viscometer at 30°C and the intrinsic viscosity was calculated by a one-point formula. The SEC column was packed with porous silica beads and toluene was used as eluent. The instrument spreading correction was applied on the average molecular weights and intrinsic viscosity calculated from the SEC chromatogram^[8]. The spreading factor of the column was calibrated with characterized narrow MWD polystyrene standards^[9].

Keywords:

Polybutadiene; Lanthanide catalyst; Molecular weight distribution; Mechanism of polymerization

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