

THE MOLECULAR WEIGHT AND ITS DISTRIBUTION OF 1,2-POLYBUTADIENES PREPARED WITH MOLYBDENUM CATALYST SYSTEMS*

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ABSTRACT

The study on the molecular weight and its distribution of 1,2-polybutadienes prepared with $\text{MoCl}_4\text{OR}-i\text{-Bu}_2\text{AlOR}'$ catalyst systems has been carried out by viscosity and GPC methods. 1,2-Polybutadienes with $\bar{M}_w/\bar{M}_n \approx 1.2-2.0$ can be obtained with these catalyst systems at 30–70°C. There is a linear relation between the $\bar{M}_w/\bar{M}_n$ and the polymerization temperature. It was found by extrapolation that these catalyst systems may possibly initiate a living polymerization at the temperature near -18°C. The molecular weight of the polymers can be regulated either by polymerization temperature or by adding polar compounds such as allyl halides.

Molybdenum catalyst systems are often used to prepare 1,2-polybutadienes^[1-3]. In this work, the investigation on the molecular weight and its distribution of 1,2-polybutadienes prepared with $\text{MoCl}_4\text{OR}-i\text{-Bu}_2\text{AlOR}'$ catalyst has been carried out by means of viscosity and GPC methods and the methods of regulation of the molecular weight and its distribution of the polymers has been searched.

EXPERIMENTAL

1,2-Polybutadiene samples are prepared in hexane with $\text{MoCl}_4\text{OR}-i\text{-Bu}_2\text{AlOR}'$ as catalyst (R, R' = allyl, aralkyl, aryl or naphthenic group). The intrinsic viscosity of the polymers was measured in toluene at 30°C by Ubbelohde viscosimeter and the molecular weight of the polymers was calculated according to

$$[\eta]_{\text{toluene}}^{30^\circ\text{C}} = 1.81 \times 10^{-4} \bar{M}_w^{0.734} [4]$$

GPC measurement was performed following reference [4].

Methods of determining microstructure were presented in the previous paper^[5].

The polar additives used in this work are of analytically pure grade.

RESULTS AND DISCUSSION

1. Factors affecting the molecular weight of the polymers

(1) The amount of MoCl_4OR The molecular weight of 1,2-polybutadienes prepared

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with $\text{MoCl}_4\text{OR}-i\text{-Bu}_2\text{AlOR}'$ is governed by the amount of MoCl_4OR added. From Fig. 1 it can be seen that the molecular weight of the polymers increases with the decrease of Mo/Bd (molar ratio of MoCl_4OR to butadiene added).

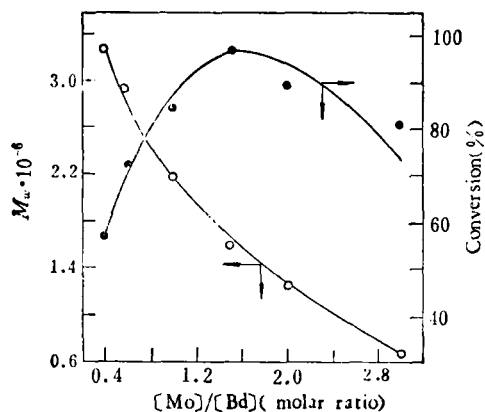


Fig. 1 Molecular weight of the polymers vs. the amount of MoCl_4OR . Polymerization conditions: 14g butadiene/100 ml; 50°C ; 9hrs. $\text{Al/Bd} = 1.28 \times 10^{-3}$.

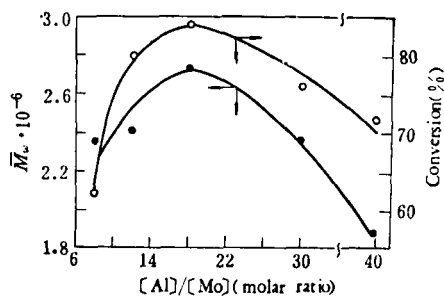


Fig. 2 Molecular weight of the polymers vs. the amount of $i\text{-Bu}_2\text{AlOR}'$. Polymerization conditions are the same as Fig. 1. $\text{Mo/Bd} = 1 \times 10^{-4}$.

(2) The amount of $i\text{-Bu}_2\text{AlOR}'$ There appears a peak in the plot of molecular weight of the polymers versus the amount of $i\text{-Bu}_2\text{AlOR}'$ added (Fig. 2). This shows that the chain transfer of aluminium alkyl in these catalyst systems is very weak.

(3) Polymerization condition A peak value in the plot of molecular weight of the polymers vs. polymerization temperature was obtained (Fig. 3), in sharp contrast to the rule that the molecular weight of polymers usually decreases with increasing polymerization temperature for polymers prepared with usual Ziegler-Natta catalyst systems. These results further imply that the chain transfer in the catalyst systems studied is difficult to occur unless at high temperature.

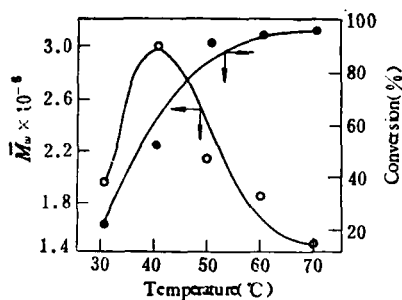


Fig. 3 Polymerization temperature dependence of molecular weight of the polymers. Polymerization conditions are the same as Fig. 1. $\text{Mo/Bd} = 1 \times 10^{-4}$; $\text{Al/Mo} = 16$.

2. Regulation of molecular weight of the polymers

As shown above, the molecular weight of polymers prepared with $\text{MoCl}_4\text{OR}-i\text{-Bu}_2\text{AlOR}'$ is very high and grows rapidly with the decrease of amount of the catalyst. Besides, gel appears in the polymers when the value of Mo/Bd is dropped to the order of 10^{-5} . These will do harm to the processing and utilization of the polymers, therefore it is necessary to control molecular weight of the polymers. In fact, all of the three polymerization conditions above can be used for this purpose, and the most effective one seems to be the adjustment of polymerization temperature. High temperature not only leads to a decrease in molecular weight but also an increase in the activity of the catalyst studied.

The molecular weight of the polymers can also be regulated by addition of some polar additives. Table 1 shows the influence of some polar additives on the molecular weight of the polymers, as can be seen from Fig. 4 and Fig. 5, allyl halides are very effective for regulating molecular weight of the polymers, among them allyl iodide being the most effective. It is of interest to note that allyl iodide is able to increase the polymerization activity of the catalyst while molecular weight of the polymers decreases within a certain limit of the amount of the catalyst used.

Table 1 Influence of polar additives on the molecular weight of polymer

Additive	[Additive]/[Mo] (molar ratio)	Conversion (%)	$\bar{M}_w \cdot 10^{-6}$
Iodide	0	81	2.66
	0.1	64	2.43
	0.2	51	2.38
	0.3	51	2.21
	0.5	38	1.68
	0.6	36	1.69
	1.0	25	1.26
	4.0	6	0.66
Trifluoacetic acid	1	60	2.59
	6	45	2.29
	8	43	2.11
	10	33	2.04
Hexachloropropylene	1	69	2.10
	2	63	2.23
	4	72	2.04
	6	63	1.91
	8	59	1.84
	10	50	1.75
Allyl benzoate	1	76	2.35
	4	74	1.97
	8	64	1.80
	10	60	1.51
Phenyl ether	1	85	2.48
	4	77	2.44
	8	80	2.34
	10	70	2.01

$\text{Mo/Bd} = 8 \times 10^{-5}$.

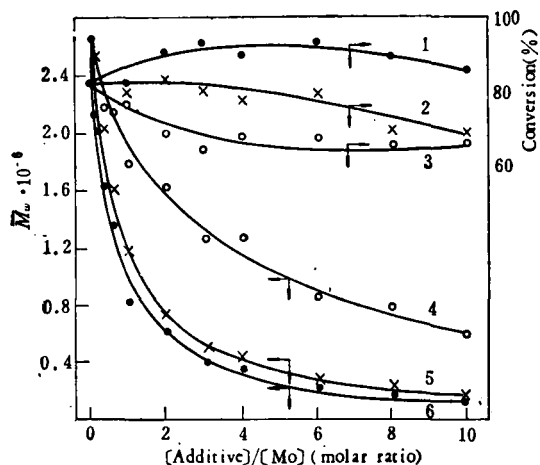


Fig. 4 Effect of allyl halides on the molecular weight of polymers
 $\text{Mo/Bd} = 8 \times 10^{-3}$, $\text{Al/Mo} = 16$.
 ●—●: $\text{CH}_2=\text{CH}-\text{CH}_2\text{I}$,
 ×—×: $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$, $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$.

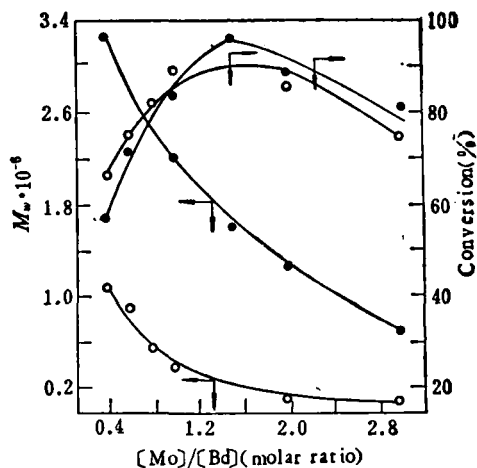


Fig. 5 Effect of allyl iodide on the molecular weight of polymers
 $\text{Al/Bd} = 1.28 \times 10^{-2}$.
 ○—○: $[\text{Allyl iodide}]/[\text{Mo}] = 2$;
 ●—●: $[\text{Allyl iodide}]/[\text{Mo}] = 0$.

3. Molecular weight distribution of the polymers

The molecular weight distribution of polymers prepared with molybdenum catalyst systems is very narrow and there is a linear relation between the $\bar{M}_w/\bar{M}_n$ and the polymerization temperature. By extrapolation it was found that at the temperature near -18°C these catalyst systems may possibly initiate a living polymerization (Fig. 6 and Fig. 7). The molecular weight distribution of the polymers can also be regulated by addition of polar additives, for example, allyl iodide (Fig. 8 and Table 2).

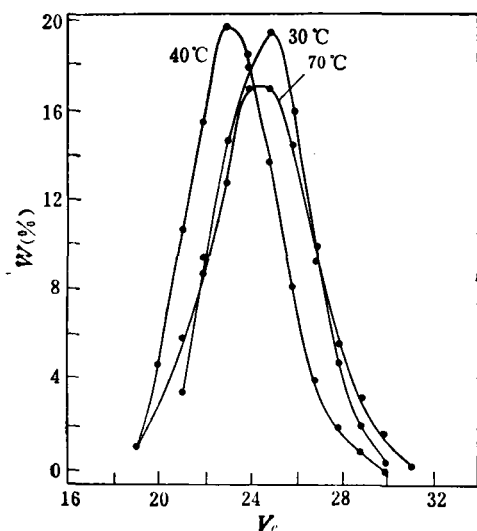


Fig. 6 GPC curves of the polymers

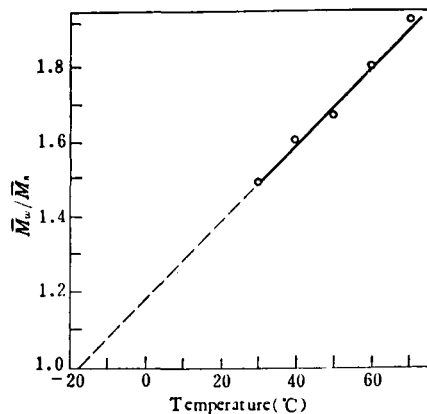


Fig. 7 Relation between polydispersity of the polymers and polymerization temperature

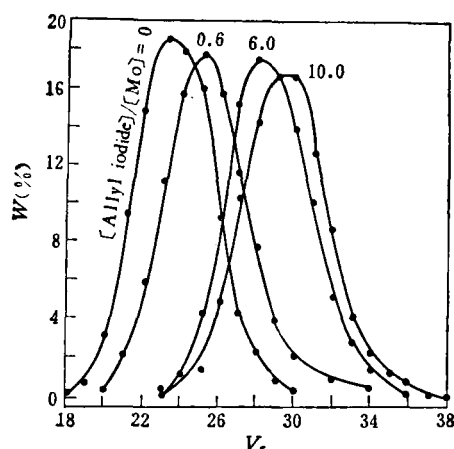


Fig. 8 Influence of allyl iodide on the molecular weight distribution of polymers

Table 2 Polydispersity of molecular weight of the polymers with allyl iodide as a additive

[Allyl iodide]/[Mo] (molar ratio)	0	0.6	1.2	3	6	10
$\overline{M}_w \cdot 10^{-6}$	2.42	1.19	1.02	0.66	0.29	0.21
$\overline{M}_n \cdot 10^{-6}$	1.49	0.50	0.40	0.30	0.13	0.09
$\overline{M}_w/\overline{M}_n$	1.62	2.38	2.56	2.20	2.23	2.23

Mo/Bd = 8×10^{-4} , Al/Mo = 16.

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