

STUDY ON SYNTHESIS OF HIGH VINYL POLYBUTADIENE WITH TETRAVALENT MOLYBDENUM CATALYST SYSTEM

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ABSTRACT

In this paper the catalytic behaviour of tetravalent molybdenum catalyst system in polymerization of butadiene is dealt with. The effects of the variety of anions combined with molybdenum atom, the pattern of the substituent R in $(i\text{-Bu})_2\text{AlOR}$ and the polymerization conditions on the butadiene conversion, the molecular weight and its distribution and the microstructure of the polymer also are studied. It has been found that the catalyst system is significantly active when anions combined with the molybdenum atom are acetoxy (CH_3COO^-) or ethoxy ($\text{C}_2\text{H}_5\text{O}^-$). Obviously, the variety of substituent R in $(i\text{-Bu})_2\text{AlOR}$ has a great influence on the catalytic activity. The catalyst system is inactive if the R group is $-\text{COR}'$ (R' is alkyl or aromatic group) or alkyl, whereas the activity of the catalyst system increases if the R group is phenyl or tolyl. With the rise of polymerization temperature the polymer molecular weight decreases, the distribution index of molecular weight increases and the content of 1,2-unit in polybutadiene reduces.

The synthesis of high vinyl polybutadiene with pentavalent molybdenum as catalyst system have been reported a lot at home and abroad^[1-4]. But the tetravalent molybdenum catalyst system used for polymerization of butadiene has seldom been reported so far. Based on the experimental results of the earlier work on the pentavalent molybdenum catalyst system, this paper deals with the polymerization of butadiene with tetravalent molybdenum as catalyst system and hydrogenated gasoline as solvent. The molecular weight and microstructure of the polymer have also been studied.

1. Effect of anions on polymerization

The effect of anions combined with the molybdenum atom on polymerization of butadiene with $(i\text{-Bu})_2\text{AlO}-\langle \bigcirc \rangle$ as co-catalyst at different Al/Mo molar ratio is studied. The results are shown as in Figure 1 and Figure 2.

In Figure 1 it can be seen that the catalyst system possesses high activity when anions combined with molybdenum atom are CH_3COO^- and $\text{C}_2\text{H}_5\text{O}^-$, and the catalytic activity of the former is higher than that of the latter. Additionally, at the same time, the butadiene conversion controlled by Al/Mo molar ratio are much the same, i.e. the peak of butadiene conversion appears with the increase of Al/Mo molar ratio. However, it is noteworthy that the Al/Mo molar ratio which brings about the highest conversion varies with the variety of

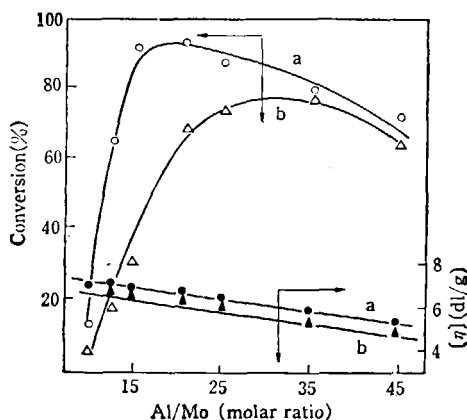


Fig. 1 Effect of variety of anions combined with molybdenum atom on the conversion and molecular weight
 a $\text{MoCl}_2(\text{CH}_3\text{COO})_2$; b $\text{MoCl}_2(\text{OC}_2\text{H}_5)_2$.
 Polymerization conditions: $\text{Mo/Bd} = 2.0 \times 10^{-4}$; 50°C ;
 7 hours; Butadiene concentration is 0.14 g/ml (the same below unless otherwise specified).

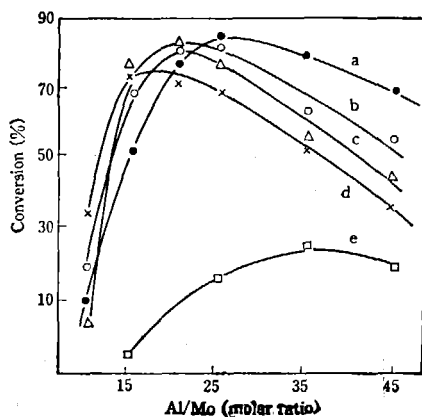


Fig. 2 Relationships between catalytic activity and the variety of R, and between catalytic activity and the carbon atom number of R in $\text{MoCl}_2(\text{RCOO})_2$

a R is $-\text{C}_3\text{H}_7$; b R is $-\text{C}_7\text{H}_{15}$; c R is $-\text{C}_{17}\text{H}_{35}$;
 d R is $-\text{C}_6\text{H}_5$; e R is $-\text{C}_6\text{H}_4\text{NO}_2$.

the anion. And the variety of anion combined with molybdenum atom has little effect on the molecular weight of polymer produced at 50°C . But the molecular weight of polymer decrease with the increase of Al/Mo molar ratio in both catalyst system.

Figure 2 shows that the catalytic activity of $\text{MoCl}_2(\text{RCOO})_2$ is independent of the variety of the R group (R is an alkyl or an aromatic group) and the number of carbon atom in R. But the activity of the catalyst system is very low when the R group is $-\text{C}_6\text{H}_4\text{NO}_2$. The reason

is likely to be connected with the existence of the electron-withdrawing group $-\text{NO}_2$.

2. Effect of the R group in $(i\text{-Bu})_2\text{AlOR}$ on polymerization

(1) R is an alkyl

The catalytic activity of $\text{MoCl}_2(\text{C}_7\text{H}_{15}\text{COO})_2-(i\text{-Bu})_2\text{AlOR}$ catalyst system will be very low when R group are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, n-amyl, sec-amyl, i-amyl, n-octyl and n-nonyl. Almost no polymer is formed after 7 hours polymerization under the conditions in which Mo/Bd molar ratio is 2.0×10^{-4} , polymerization temperature 50°C , Al/Mo molar ratios 10, 20 and 30 respectively. It is shown that the catalyst and co-catalyst can not match. This result is different from the case with the pentavalent molybdenum catalyst system^[5]. And the cause remains to be studied.

(2) R is $-\text{COR}'$ (R' is an alkyl or an aromatic group)

The polymerization of butadiene can not yet be initiated in the same polymerization conditions as mentioned above when R' are $-\text{H}$, $-\text{CH}_3$, $-\text{C}_3\text{H}_7$, $-\text{C}_7\text{H}_{15}$, $-\text{C}_6\text{H}_5$ group, etc. It is shown that the catalyst system made of $\text{MoCl}_2(\text{C}_7\text{H}_{15}\text{COO})_2$ and $(i\text{-Bu})_2\text{AlCOOR}'$ is inactive.

(3) R is an aromatic group

Of high activity is the catalyst system made of $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4$ and $\text{MoCl}_2(\text{RCOO})_2$ or $\text{MoCl}_2(\text{OR})_2$ (see Fig. 1 and Fig. 2). It is probable that after the formation of an active centre, the non-bonding d-orbit in the central molybdenum atom has conjugated with $-\text{O}-\text{C}_6\text{H}_4$, thus increases electronic density of the molybdenum atom. To justify the above point of view, we have respectively examined the catalytic activity of the catalyst system made of $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4-\text{NO}_2$, $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4$, and $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4-\text{CH}_3$ with $\text{MoCl}_2(\text{C}_7\text{H}_{15}\text{COO})_2$ for butadiene polymerization. The result is shown in Figure 3. And it

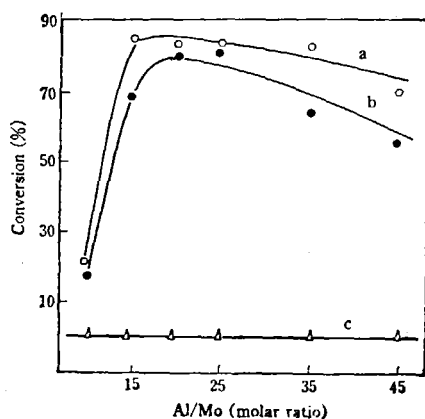


Fig. 3 Effect of Ar in $(i\text{-Bu})_2\text{AlOAr}$ on catalytic activity

a Ar is $-\text{C}_6\text{H}_4-\text{CH}_3$; b Ar is $-\text{C}_6\text{H}_4$; c Ar is $-\text{C}_6\text{H}_4-\text{NO}_2$.

indicates that when the aromatic group is $\text{—}\langle\bigcirc\rangle\text{—NO}_2$ the catalyst system is still inactive. The reason is that the —NO_2 is a strong electron-withdrawing group which decreases the electronic density in central molybdenum atom and the active species is difficult to form. On the contrary, the catalytic activity of the catalyst system with the aromatic group $\text{—}\langle\bigcirc\rangle\text{—CH}_3$ is higher than that of with $\text{—}\langle\bigcirc\rangle\text{—}$. Clearly, it is attributed to the electron-donating group —CH_3 .

The above recited experimental results not only make a contribution to elucidate the reaction mechanism, but also offer some suggestions for finding a high active molybdenum catalyst system.

3. Effect of polymerization temperature on polymerization

Figure 4 shows that the effect of polymerization temperature on the polymerization rate is very remarkable. When the polymerization temperature is 40°C , the butadiene conversion is only 70% in 24 hours. If the polymerization temperature is raised to 50°C , the butadiene conversion is over 80% in 5 hours. When polymerization temperature is high, polymerization rate appears as an attenuating type, i.e. the former part of the period is of a higher speed and the latter of a lower speed. When polymerization temperature is low, polymerization rate decreases very little and the conversion of butadiene almost sharply rises with the increasing of polymerization time (see curve c).

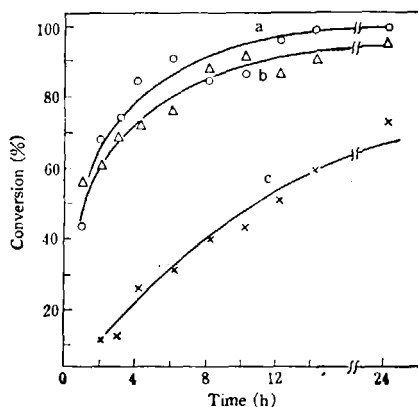


Fig. 4 Relationship between polymerization temperature and polymerization rate for $\text{MoCl}_2(\text{C}_7\text{H}_{14}\text{COO})_2\text{—}(\text{i-Bu})_2\text{AlO—}\langle\bigcirc\rangle$ catalyst system, $\text{Al/Mo}=15$
a 50°C ; b 60°C ; c 40°C .

In Figure 5 it can be seen that at 40°C , even though Mo/Bd molar ratio is 3.2×10^{-4} , the butadiene conversion is below 80% in 7 hours; if the polymerization temperature is up to 50°C while Mo/Bd molar ratio reduced to 1.6×10^{-4} , the butadiene conversion will be over 80% in 7 hours, i.e. in order to reach the same conversion, if polymerization temperature is increased by 10°C , the quantity of catalyst used is decreased to the half of the original. But when the

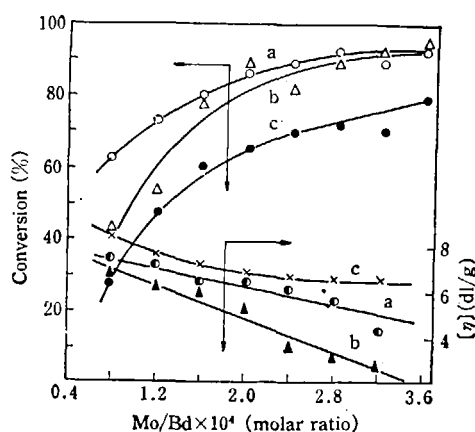


Fig. 5 Relationships between temperature and conversion, and between temperature and molecular weight for $\text{MoCl}_2(\text{C}_7\text{H}_{15}\text{COO})_2-(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4-\text{CH}_3$ catalyst system, $\text{Al}/\text{Mo}=20/$
 a 50°C ; b 60°C ; c 40°C

polymerization temperature goes up to 60°C , the butadiene conversion drops instead.

The polymerization temperature effects not only the catalytic activity but the molecular weight of the polymer and its distribution as well (see Figure 5 and Table 1). When the polymerization temperature is raised, the molecular weight decreases and the distribution index of the molecular weight increases. These results show that the polymerization temperature, to a certain extent, can be used as the means for regulating molecular weight and its distribution.

Table 1 Molecular weight and its distribution index obtained by GPC

Catalyst system	Temperature ($^\circ\text{C}$)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
$\text{MoCl}_2(\text{C}_7\text{H}_{15}\text{COO})_2-$ $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4-\text{CH}_3$	40	171	64	2.7
	50	159	54	3.1
	60	158	49	3.2
$\text{MoCl}_2(\text{OC}_8\text{H}_{17})_2-$ $(i\text{-Bu})_2\text{AlO}-\text{C}_6\text{H}_4-\text{CH}_3$	25	174	64	2.7
	35	183	59	3.1
	70	138	31	4.5

4. Microstructure of the polymer

The IR measurement of microstructure of the polymer represents that the size and variety of the R group in $\text{MoCl}_2(\text{RCOO})_2$ and the molar ratio of catalyst and co-catalyst have no

any effects on the ways in which monomer inserts into a growing chain although the polymerization temperature makes a little difference to microstructure of the polymer (see Figure 6). The content of 1,2-unit in polybutadiene will be over 80% and *cis* 1,4-unit is scarcely contained.

The relative content of various stereoisomers of 1,2-unit and their sequence lengths in polybutadiene obtained according to the previous paper^[6] by way of ¹³C-NMR are shown in Table 2. The results show that the highest is the content of isotactic stereoisomer among the various stereoisomer of 1,2-unit in polybutadiene synthesized by the tetravalent molybdenum catalyst system and that uniform are the sequence lengths of the various stereoisomers.

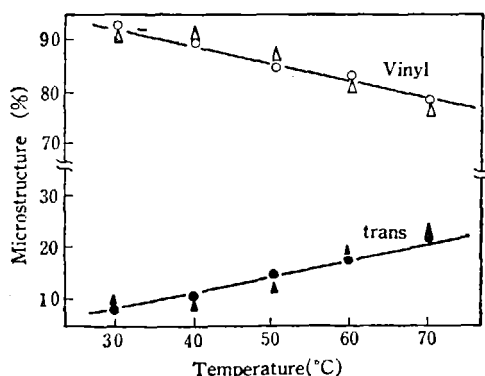


Fig. 6 Effect of the polymerization temperature on microstructure of the polybutadiene synthesized by the $\text{MoCl}_5(\text{RCOO})_3$ -(*i*-Bu)₂AlO- catalyst system
○, ● R is -C₇H₁₅; △, ▲ R is -CH₃.

Table 2 Relative content of various stereoisomer of 1,2-unit and their sequence distribution in polybutadiene synthesized by the $\text{MoCl}_5(\text{RCOO})_3$ -(*i*-Bu)₂AlO-

R	Content of various stereoisomers (%)			Number average sequence length and weight average sequence length				Sequence distribution of stereoisomer	
	P _i	P _a	P _s	$\langle M_i \rangle_n$	$\langle M_s \rangle_n$	$\langle M_i \rangle_w$	$\langle M_s \rangle_w$	$\langle M_i \rangle_w / \langle M_i \rangle_n$	$\langle M_s \rangle_w / \langle M_s \rangle_n$
-CH ₃	58	37	5	4.2	1.3	7.3	1.6	1.7	1.2
-C ₃ H ₇	60	35	5	4.5	1.3	8.0	1.6	1.8	1.2
-C ₇ H ₁₅	58	32	10	4.1	1.3	7.3	1.6	1.8	1.2

* P_i isotactic; P_a atactic; P_s syndiotactic.

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