

A STUDY OF POLYBUTADIENE SYNTHESIS WITH $\text{MoCl}_n(\text{OR})_{4-n}(\text{i-Bu})_2\text{AlOPh}$ AS A CATALYST

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ABSTRACT

The catalytic effect of $\text{MoCl}_n(\text{OR})_{4-n}(\text{i-Bu})_2\text{AlOPh}$ on the polymerization of butadiene in hydrogenated gasoline is studied (R is alkyl, cycloheptyl, phenyl of C_{4-16}). In this system, the solubility and the catalytic activity of the catalyst do not depend on whether the number of carbon atoms in R group is odd or even. The R group with the primary and secondary carbon atom has a fairly great influence on the catalytic activity. When R is an alkyl, the catalytic activity increases and the range of Al/Mo values that keeps higher conversion of butadiene is broadened as the size of the R group increases. The content of 1,2-units in the polymer hardly varies with the size of the R group.

The work of polybutadiene synthesis with $\text{MoCl}_n(\text{OC}_8\text{H}_{17})_{4-n}(\text{i-Bu})_2\text{AlOPh}$ as a catalyst has been reported in a previous paper^[1]. It is found that the solubility of $\text{MoCl}_n(\text{OC}_8\text{H}_{17})_{4-n}$ in hydrogenated gasoline is higher than that of MoCl_4 ^[2], and its catalytic activity also increases. This article deals with the solubility of $\text{MoCl}_n(\text{OR})_{4-n}$ in hydrogenated gasoline and the relationship between its catalytic effect and the R group. The effects of both the quantities of the catalyst and cocatalyst and the ratio between them on the catalytic activity, the molecular weights of the polymer and their distribution are also studied. The microstructure of the polybutadiene is determined by the IR method.

The purification of butadiene (Bd), hydrogenated gasoline, and the preparation of the catalyst and the experimental operations were carrying out as previously reported^[1].

The molecular weight distribution of polybutadiene is determined with Model NJ-762 gel permeation chromatography using tetrahydrofuran as solvent. The microstructure of the polymer is determined with infrared spectrophotometry (Shimadzu IR-408)^[3].

1. The solubility of $\text{MoCl}_n(\text{OR})_{4-n}$

MoCl_4 reacts with alcohol, phenol that carry alkyl, cycloheptyl phenyl of C_{1-16} as an R group respectively. The results show that the smaller the number of carbon atom in the R group, the faster the reaction. With the hydrogenated gasoline added, the yielded catalyst is insoluble if the carbon number of the alkyl is smaller than 4; the solubility of the catalyst whose R group is isobutyl is higher than that of n-butyl; the solubility is very good if the carbon number in the alkyl R group is larger than 5; and the solubility is poor if the R group is cycloheptyl, phenyl or benzyl. Adding a small amount of EA to the reactant resulting from MoCl_4 and hexalin, the solubility and the catalytic activity of the reactant increase. Whereas in

the case of MoCl_4 and benzyl alcohol, both the solubility and the catalytic activity decrease.

The experimental results show that the temperature also influences the solubility of the catalyst. The solubility changes favorably when temperature goes up. At room temperature, white sediment will separated out from the solution of $\text{MoCl}_n(\text{OC}_{18}\text{H}_{33})_{4-n}$ and the sediment will dissolve upon heating.

2. The relationship between R group and the catalytic effect of $\text{MoCl}_n(\text{OR})_{4-n}$

Butadiene is polymerized into polybutadiene with soluble $\text{MoCl}_n(\text{OR})_{4-n}$ (abbreviated to Mo) as a catalyst and $(i\text{-Bu})_2\text{AlOPh}$ (abbreviated Al) as a cocatalyst. It is shown that the percentage conversion of butadiene attains a peak value at a certain Al/Mo molar ratio. For different R groups both the conversion curves and the positions of the peak are different (see Fig. 1 and Fig. 2).

As shown in Fig. 1 and Fig. 2, the catalytic activity of $\text{MoCl}_n(\text{t-OC}_7\text{H}_{15})_{4-n}$ is the lowest, and $\text{MoCl}_n(\text{s-OC}_5\text{H}_{11})_{4-n}$ is more active, whereas the activity of $\text{MoCl}_n(\text{OR})_{4-n}$ carrying n-alkyl and iso-alkyl as R group is the highest. That is to say, the catalytic rank of the primary alcohol is the highest while the secondary is higher than the tertiary.

The difference^[4] from the system of the five valence molybdenum is that in this system the catalytic activity of iso-alkyl is higher than that of n-alkyl, and that the solubility and the catalytic activity of the catalyst are not depending on whether the number of the carbon atoms in the R group is odd or even. The conversion of butadiene for various R group is higher than that of the five valence molybdenum system; at the same conversion, Al quantity needed is lesser. The range of Al/Mo molar ratio that keeps a higher conversion

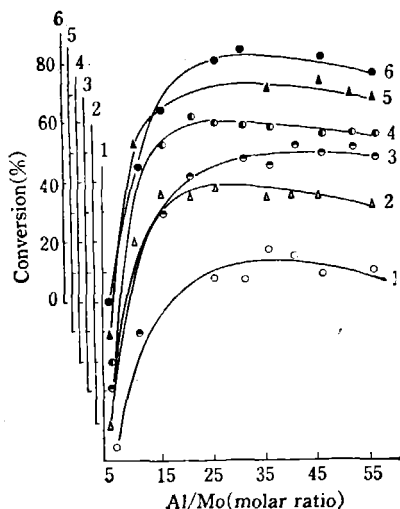


Fig. 1 The effect of Al/Mo molar ratio on the conversion of butadiene

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|---|---|
| 1. $\text{MoCl}_n(\text{OC}_4\text{H}_9)_{4-n}$; | 2. $\text{MoCl}_n(\text{OC}_6\text{H}_{13})_{4-n}$; |
| 3. $\text{MoCl}_n(\text{OC}_8\text{H}_{17})_{4-n}$; | 4. $\text{MoCl}_n(\text{OC}_9\text{H}_{19})_{4-n}$; |
| 5. $\text{MoCl}_n(\text{OC}_{10}\text{H}_{21})_{4-n}$; | 6. $\text{MoCl}_n(\text{OC}_{18}\text{H}_{33})_{4-n}$. |

$\text{ROH/Mo}=8$; $\text{Mo/Bd}=2.0 \times 10^{-4}$; 50°C ; 7 hr.

(The same below, unless otherwise specified)

of butadiene is rather broad. The change of R group has a rather petty influence on both the molecular weights and their distribution of the polymer (see Fig. 2 and Fig. 3 and Table 1).

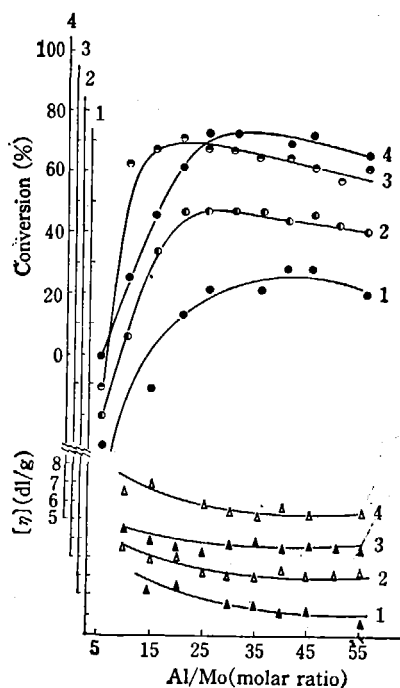


Fig. 2 The effect of Al/Mo molar ratio on the conversion of butadiene and $[\eta]$

1. $\text{MoCl}_n(\text{t-OC}_7\text{H}_{15})_{4-n}$; 2. $\text{MoCl}_n(\text{s-OC}_8\text{H}_{17})_{4-n}$;
3. $\text{MoCl}_n(\text{t-OC}_8\text{H}_{17})_{4-n}$; 4. $\text{MoCl}_n(\text{i-OC}_8\text{H}_{17})_{4-n}$.

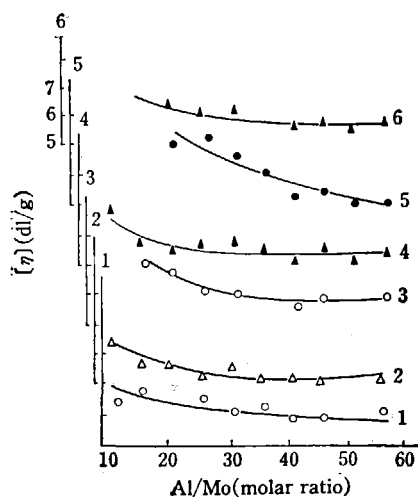


Fig. 3 The effect of Al/Mo molar ratio on $[\eta]$
(See also the note of Fig. 1)

From Fig. 2 and Fig. 3 it can be seen that Al/Mo molar ratio has a little influence on the molecular weights of the polymer, if Al/Mo molar ratio is small, $[\eta]$ decreases slightly as the Al/Mo molar ratio increases. When Al/Mo molar ratio is more than 30, $[\eta]$ does not change appreciably. This indicates that reaction of chain transfer to Al is very little.

Table 1 The effect of the R group on the index of the width of the molecular weight distribution

R group	Mo/Bd $\times 10^4$	Al/Mo* (molar ratio)	$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
n-C ₄ H ₉	2.0	35	1.83	5.9	3.09
i-C ₄ H ₉	2.0	25	1.86	6.9	2.69
n-C ₅ H ₁₁	2.0	30	1.81	4.7	3.81
i-C ₅ H ₁₁	2.0	20	1.57	5.3	2.97
t-C ₇ H ₁₅	2.0	40	1.94	6.9	2.79
n-C ₈ H ₁₇	2.0	50	1.75	5.7	3.10
n-C ₉ H ₁₉	2.0	20	1.48	4.6	3.19
n-C ₁₀ H ₂₁	2.0	45	1.69	6.2	2.69
n-C ₁₆ H ₃₃	2.0	30	1.86	6.4	2.94

* Al/Mo molar ratio at the highest conversion.

3. *The relationship between catalytic activity and the quantity of $\text{MoCl}_n(\text{OR})_{4-n}$ used as catalyst*

As seen in Fig. 4, the conversion of butadiene varies directly with the amount of Mo.

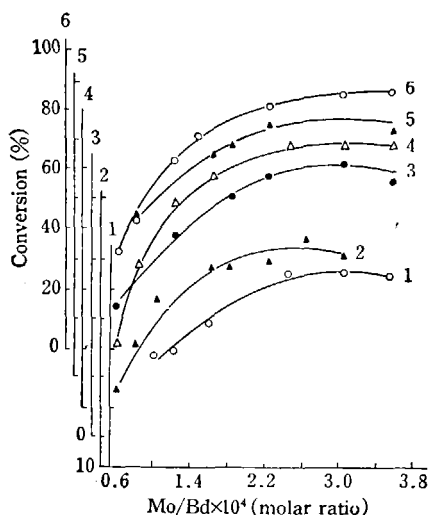


Fig. 4 The effect of Mo on the catalytic activity
(see also the note of Fig. 1)
Al/Mo = 4.0×10^{-3} (the same below)

The change for different R groups are similar to each other. If the R group is *n*-alkyl, the conversion of butadiene will be above 80%, with Mo/Bd molar ratio being 2.0×10^{-4} . The catalytic activity rises a little when the size of the R group increases.

The catalytic activity of several catalysts varying with a branch chain in the R group is shown in Fig. 5. The catalytic activity of $\text{MoCl}_n(\text{OR})_{4-n}$ is different when it is replaced by the primary, secondary or tertiary alcohol. The result conforms to the case with Fig. 1 and Fig. 2.

Mo quantity has a great influence on the molecular weights. $[\eta]$ reduces when the Mo/Bd molar ratio goes up (see Fig. 5 and Fig. 6), and $[\eta]$ is slightly lower in the case that R group is *n*-alkyl.

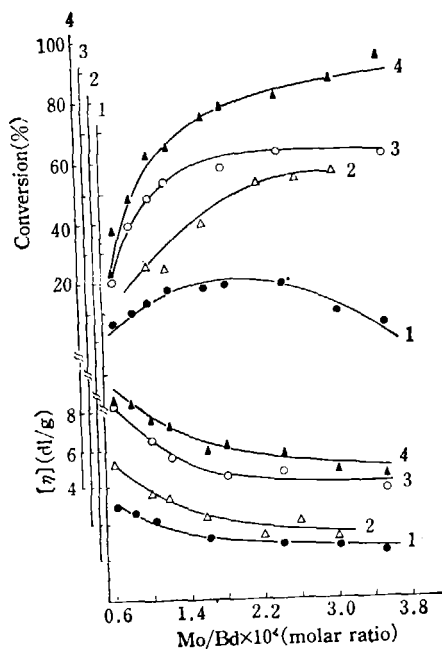


Fig. 5 The effect of Mo on conversion and $[\eta]$ (see also the note of Fig. 2)

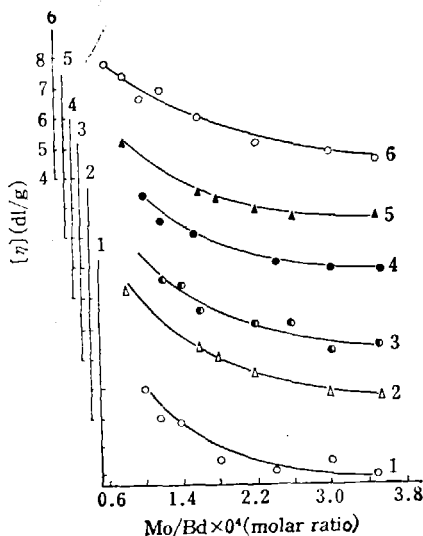


Fig. 6 The effect of Mo on $[\eta]$ (see also the note of Fig. 1)

4. The microstructure of the polymer

Table 2 illustrates the microstructure of the polymer yielded by the use of catalyst with various R groups. It is clear from the table that the changing of the R group makes only slight difference to the microstructure of the polymer. It is shown that almost no *cis* 1,4-units exists, while the content of *trans* 1,4-units is about 10%. The majority of the contents is 1,2-units, generally above 80%.

Table 2 The effect of the R group on the microstructure of polymer

R group	Al/Mo* (molar ratio)	Microstructure of polymer (%)		
		<i>cis</i> 1,4-	1,2-	<i>trans</i> 1,4-
n-C ₄ H ₉	35	0	91	9
i-C ₄ H ₉	25	0	89	11
n-C ₅ H ₁₁	30	0	88	12
i-C ₅ H ₁₁	20	1	82	17
s-C ₅ H ₁₁	25	1	88	11
t-C ₇ H ₁₅	40	0	91	9
n-C ₆ H ₁₃	50	0	90	10
n-C ₈ H ₁₇	20	0	93	7
n-C ₁₀ H ₂₁	45	0	91	9
n-C ₁₆ H ₃₃	30	1	90	9

* Al/Mo molar ratio at the highest conversion.

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