

CHARACTERIZATION OF IRON COMPLEXES SUPPORTED ON POLYMER AND THEIR CATALYTIC ACTIVITY IN BUTADIENE POLYMERIZATION

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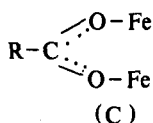
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ABSTRACT

Styrene-acrylic acid copolymer (SAAC)-supported iron complex (SAAC · Fe) was characterized and the effect of the characteristic parameters on the catalytic activity of the complex was investigated. IR spectrum suggested that the complex SAAC · Fe possesses a structure of (C) and the Fe—O bond is higher in covalency.



The complex SAAC · Fe with the structure of (C) showed a higher catalytic activity in butadiene polymerization. When Fe/—COOH molar ratio in SAAC · Fe was about 0.2 the complex gave optimum catalytic activity. The catalytic activity of SAAC · Fe with the higher content of long sequence of acrylic acid units was low. When the content of the short sequence of acrylic acid units was predominant and at the same time the content of the short sequence was approximately equal to that of the long sequence for styrene, the activity of the complex was high.

The use of polymer-supported iron complex system in butadiene polymerization had been reported^[1].

It is well known that the efficiency of the catalyst is influenced by the nature, the valence state of the transition metal, the type of ligands attached to the transition metal, and the catalyst morphology, etc. Varying the ligands attached to the metal can change the distribution of the electron density of the metal (i. e. the bond polarity) in the active species so that the catalyst activity is effected. The situation will become more complicated when polymer replaces low molecular weight compound as the ligand. Our aim in this paper is to characterize the iron complexes supported on styrene-acrylic acid copolymer and investigate the effect of the characteristic parameters, such as the sequence distribution of monomeric units in the copolymer and the constitution of the complexes, on the catalytic activity.

EXPERIMENTAL

Materials

Analytically pure grade toluene was refluxed with K—Na alloy and distilled before use. Commercially pure grade hexane was dried over active alumina for a week.

Analytically pure grade iron chloride was used. A certain concentration solution of phenanthroline (Phen) in toluene was prepared before use. Triisobutylaluminum was obtained from Fluka AG.. Butadiene was dried over active alumina. The styrene-acrylic acid copolymer (SAAC) was prepared according to the literature²¹.

Preparation of Iron complex supported on styrene-acrylic acid copolymer (SAAC · Fe)

A solution of iron chloride in methanol was added to a solution of SAAC in methyl ethyl ketone (MEK) at room temperature. Then a solution of ammonium hydroxide in MEK was added dropwise into the mixture with stirring. After this, the reaction system was allowed to stand for 1h. The product, which was insoluble in the reaction medium, was filtered out immediately, washed with distilled water until no chloride ion could be detected in the filtrate, and dried under vacuum at 60 °C for 48h.

Polymerization procedure and analysis of polymer

The polymerization was carried out in 25ml ampules under Ar. Moisture and air were carefully excluded in all the polymerization processes. The polymerization was terminated by adding an ethanol solution containing phenyl-β-naphthylamine. The polymer obtained was precipitated with an excess of ethanol and dried under vacuum below 40 °C to constant weight.

The intrinsic viscosity $[\eta]$ and the microstructure of the polymer were determined according to a previously reported method^[3].

RESULTS AND DISCUSSION

Catalyst activity

The significant improvement in polymerization activity probably represents the one of the characteristics of most important advantage of the polymer-supported catalyst. The catalytic activity of SAAC · Fe system is significantly higher than those of the small molecule catalysts^[4] in Table 1. It can be seen that a practically complete conversion takes only 10 min for SAAC · Fe system. The catalytic efficiency of SAAC · Fe is up to 99kg polybutadiene/(g Fe · h), while in the case of Fe(naph)₃, which exhibits the highest activity among the low molecule iron catalysts, the productivity is 0.49kg polybutadiene/(g Fe · h). Thus, the catalyst activity of SAAC · Fe system is about 200 times that of Fe(naph)₃ system.

Table 1 Comparison of the activities of various iron catalyst systems

Catalyst system	Fe/Bd (μ mol / g)	Al/Fe (atom ratio)	Temperature (°C)	Time (min)	Conversion (%)
SAAC · Fe-Phen-Al(i-Bu) ₃	1	70	20	10	92
Fe(St) ₃ -Bpy-Al(i-Bu) ₃	4	30	Room temp.	240	9
Fe(hep) ₃ -Bpy-Al(i-Bu) ₃	4	30	Room temp.	240	41
Fe(naph) ₃ -Bpy-Al(i-Bu) ₃	4	30	Room temp.	240	44

hep = heptylate; naph = naphthenate; St = stearate.

Characteristics of iron complexes supported on styrene-acrylic acid copolymer (SAAC)

Elemental analysis of the reaction product (SAAC · Fe) of SAAC with FeCl₃ shows the absence of Cl. It is indicated that the chlorine in FeCl₃ is exchanged by the

carboxylic groups in SAAC to form macromolecular carboxylate complexes with Fe as crosslinking point. It can be seen from Figure 1 that the bands at 1700 and 1235 cm^{-1} are attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ of the carboxylic group in SAAC. New bands appear at 1583 and 1417 cm^{-1} for $\text{SAAC} \cdot \text{Fe}$, which are assigned $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ respectively. The bands at 1583 and 1417 cm^{-1} become strengthened with the increase of the content of Fe in $\text{SAAC} \cdot \text{Fe}$ whereas those at 1700 and 1235 cm^{-1} become weak.

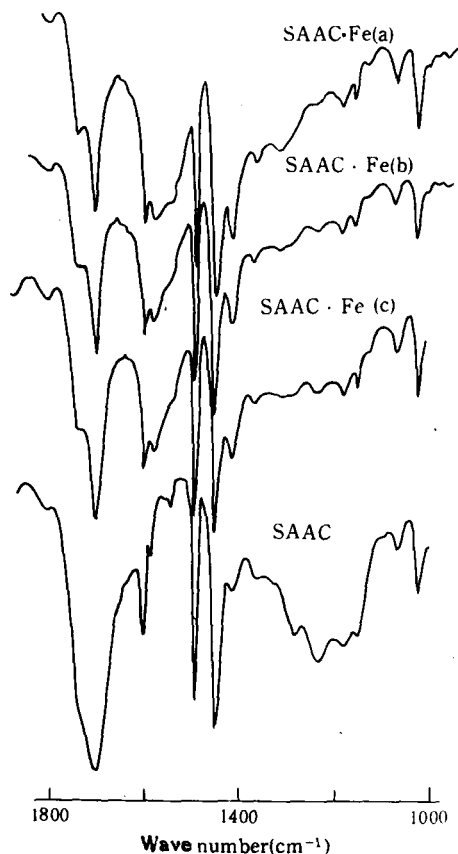
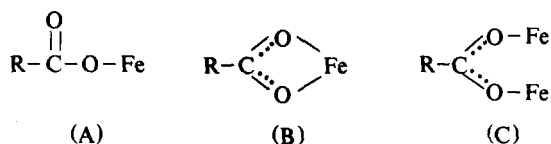


Figure 1 IR absorption spectra : SAAC and SAAC $\cdot$ Fe complex
(a). Fe=0.68 mmol/g; (b). Fe=0.51 mmol/g; (c). Fe=0.35 mmol/g.

Three modes of bonding through carboxylic group are regarded as the most probable ones in the case of $\text{SAAC} \cdot \text{Fe}$ formation :



The difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, $\Delta\nu$, reflects the symmetry of the carboxylic group on the complex formation and the bond covalency. In the case of $\text{SAAC} \cdot \text{Fe}$, $\Delta\nu$ of 166 cm^{-1} was observed. Based on the investigation of IR spectra^[5], it is possible that the complex $\text{SAAC} \cdot \text{Fe}$ possesses the structure of (C) and the Fe-O bond is higher in covalency. One of the requirements for the formation of the active center is the alkylation of iron ions by exchange between the alkyl group in

alkyl aluminum and carboxylate for the iron catalyst system used in the polymerization of butadiene. The covalency of the Fe-O in the support complex makes the exchange reaction easier. This is fully proved by higher catalytic activity of the complex in butadiene polymerization (Table 1).

Effect of the structure of the support polymers and the constitution of their metal complexes on the catalytic activity

Mayo-Lewis's equation^[6] which relates the copolymer composition to the monomer composition is given by :

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (= \frac{m_1}{m_2} \text{ for low conversions})$$

where M_1 and M_2 refer to the monomer composition and m_1 and m_2 to the polymer composition. r_1 and r_2 are the reactivity ratio of M_1 and M_2 , respectively. According to statistical theory, the probability that a sequence of m_1 units contains n members is :

$$P(m_1)_n = P_{11}^{(n-1)} (1 - P_{11}) = \left(\frac{1}{1 + \frac{1}{r_1 F}} \right)^{n-1} \frac{1}{1 + r_1 F} \quad (1)$$

Similarly :

$$P(m_2)_n = P_{22}^{(n-1)} (1 - P_{22}) = \left(\frac{1}{1 + \frac{F}{r_2}} \right)^{n-1} \frac{1}{1 + \frac{r_2}{F}} \quad (2)$$

These values represent the fraction of all the m_1 (or m_2) sequences formed by n members. Where F which is a function of the ratio (f) between the molar concentration of m_1 and m_2 in the copolymer can be obtained from the copolymerization equation written by Fineman and Ross^[7] :

$$F = \frac{f - 1 + \sqrt{(f - 1)^2 + 4 r_1 r_2 f}}{2 r_1}$$

In the copolymerization of styrene with acrylic acid, the reactivity ratio determined was 0.23 (r_S) and 0.15 (r_{AA}) by means of Fineman and Ross^[7]. The values of the distribution function P for sequences of different length for styrene-acrylic acid copolymer can be calculated from equations (1) and (2).

Figure 2 shows the values of the distribution function P for sequences of different length for styrene-acrylic acid copolymers of different composition and the catalytic activities of the iron complexes supported on the copolymers having the corresponding composition. The probability of existence of long sequences of styrene, or of acrylic acid, increases with the increase of the content of the considered monomer in the copolymer. The distribution of short sequence of styrene increases, whereas that of acrylic acid slightly decreases, with the increase of the content of acrylic acid in the copolymer. The catalytic activity of SAAC · Fe with the highest distribution of long sequences of acrylic acid is low. It is possible that the functional groups -COOH in the SAAC with the high distribution of long sequences of acrylic acid are not efficiently dispersed on the polymer chains and then the iron ions in the complexes are

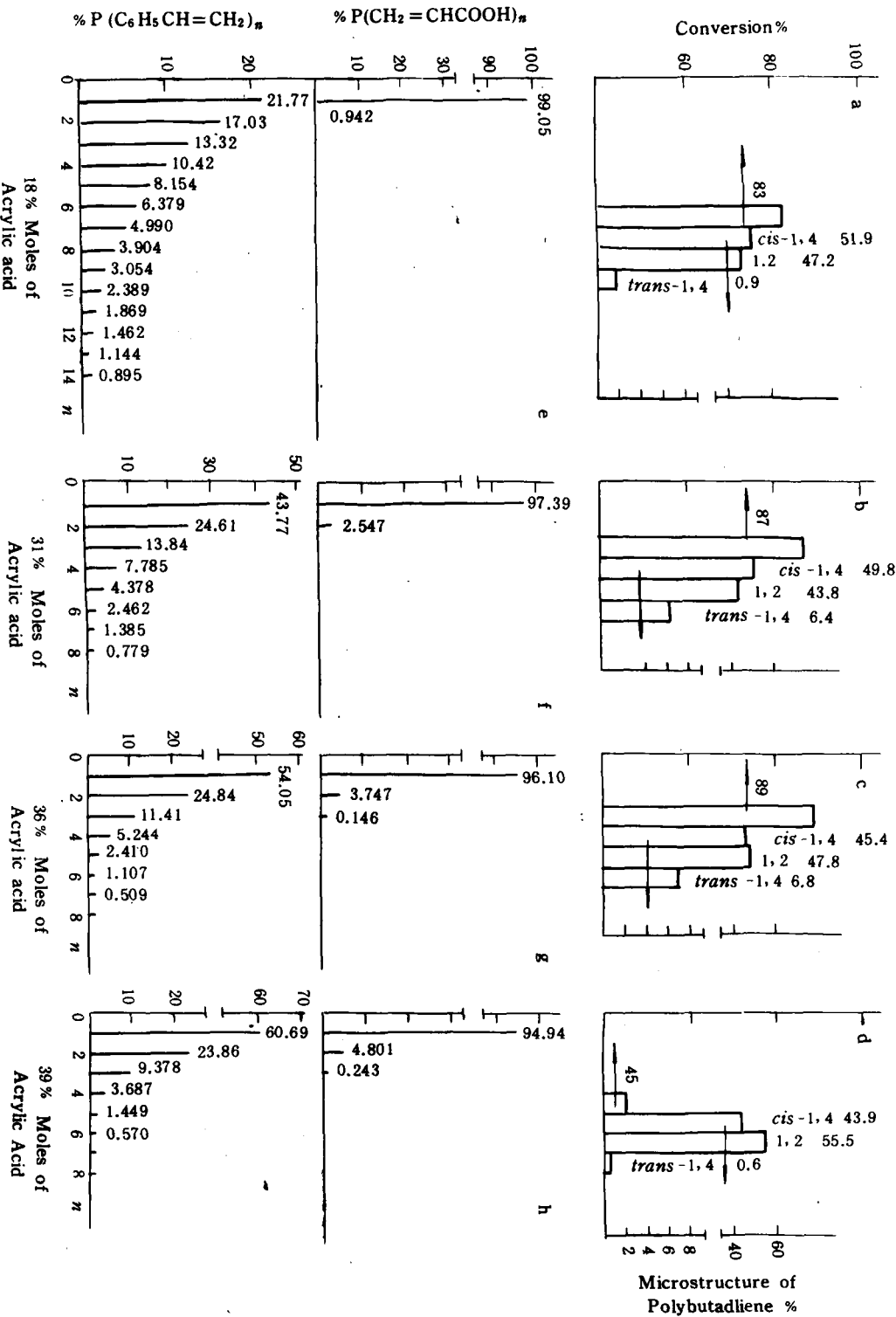


Fig. 2 Distribution function of sequences of different lengths in SAAC and activity of SAAC · Fe

difficult to contact with alkyl aluminum to form the active centers. When the distribution of short sequence of acrylic acid in the copolymers is predominant, and the short sequence distribution is approximately equal to that of long sequences for styrene, the complexes show the optimum activity. The microstructure of the polybutadiene prepared is not affected by the structure factor of the support polymer.

The activity of polymer-supported iron complexes is not only related to the structure factor of the polymer, but also to the constitution factor of the complexes. It is in-

Table 2 Effect of Fe/-COOH molar ratio on the activity

Functional group (mmol/g)	Quantity of bound metal		Conversion (%)	[η] (dl/g)
	mmol/g	mol/mol of functional group		
2.66	0.35	0.13	71	13.2
	0.42	0.16	76	11.3
	0.51	0.19	78	11.1
	0.53	0.20	81	10.6
	0.87	0.33	76	12.1

Polymerization conditions : Fe/Bd (μ mol/g) = 1 ; AL/Fe (molar ratio) = 70 ; 20 °C ; 30 min

licated in Table 2 that at high catalytic activity the Fe/-COOH molar ratio in the complexes is 0.20. As the content of the iron in SAAC · Fe increases, the catalytic activity reaches a maximum value. When the iron content is too high a portion of iron is embedded, and only the iron metal on the surface of the formed catalyst will be activated, as usually occurs in Ziegler-Natta heterogeneous catalysts. At much lower Fe content, the amount of Fe per unit support volume is very low, and less active centers formed so that the activity is low.

Keywords :

Iron Complex ; Styrene Acrylic Copolymer ; Butadiene ; Polymerization

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REFERENCES

- [1] 李玉良、逢素芬、韩冬、欧阳均, 催化学报 (*Journal of Catalysis*), **1984**, 5(2), 174.
- [2] Nikolaev A. F. and Galperin V. M. *Vysokomol. Soedin.*, **1967**, A9, 2469.
- [3] Li, Yuliang and Quyang, Jun, *J. Macromol. Sci Chem.*, **1987**, A24, 227.
- [4] 章哲彦、陈启儒, 合成橡胶工业 (*Hecheng Xiangjiao Gongye*), **1982**, 5 (5), 378.
- [5] Allcock N. W. and Tracy V. M. *J. Chem. Soc. Dalton*, **1976**, 21, 2243.
- [6] Mayo F. R. and Lewis, F. M. *J. Am. Chem. Soc.*, **1944**, 66, 1594.
- [7] Fineman M. and Ross S. D. *J. Polym. Sci.*, **1950**, 5, 259.