

# SYNTHESIS OF *cis*-1, 4-POLYBUTADIENE WITH NICKEL CATALYST INVESTIGATIONS ON INTERACTIONS BETWEEN THE CATALYTIC COMPONENTS BY USING UV-VIS SPECTRUM

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## ABSTRACT

Ni(II) naphthenate in hydrogenated gasoline or toluene will appear light green, which is the result of absorption in the red and blue bands of the spectrum. The three peaks caused by the spin-allowed d-d transitions are 403, 680, and 1170nm respectively, and are similar to those of  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$ . The configuration of Ni(II) complex is octahedral.

In a two-component system of  $\text{Ni}(\text{naph})_2\text{-Al}(\text{i-Bu})_3$ , the naphthenate ligand attached to Ni(II) can be exchanged for the alkyl group on tri-isobutylaluminium, if  $\text{Al}(\text{i-Bu})_3/\text{Ni}(\text{naph})_2$  in a system containing metalalkyl and naphthenate does not exceed the value of 0.53. At a higher ratio,  $\text{Al}(\text{i-Bu})_3/\text{Ni}(\text{naph})_2 > 0.53$ , Ni(II) is reduced to Ni(I) and Ni(O).

In a two-component system  $\text{Ni}(\text{naph})_2\text{-BF}_3\text{-OEt}_2$ , a part of the naphthenate can be exchanged for halogen. A new Ni(II) complex is formed, which consists of three new d-d bands in the region 360-1660 nm.

## INTRODUCTION

In our country, researches on synthesis of *cis*-1, 4-polybutadiene with nickel catalyst system in hydrogenated gasoline were carried out about twenty years ago. It was reported that the behaviour of the nickel catalyst system had been studied with infrared (IR), electrical conductivity<sup>[1,2]</sup> and electron spin resonance (ESR) spectroscopy<sup>[3,4]</sup>. However, some problems, such as the interactions between the components, the structure of active center, and nickel's oxidation state in the catalyst system, are worthy of getting insight.

According to the principle of ligand field theory, that the ions of transition metals give rise to a wide range of colors, which vary in hue and intensity from compound to compound and with oxidation state, has long been known to be one of their characteristic features. These colors arise from the absorption of the visible spectrum by the ions and the structure of ligand groups bound to them.

In this paper, the preliminary study on the nickel catalyst system was done with the method of UV-VIS spectrum. Results concerning the structure of Ni(II) complex and the change of the oxidation state have been obtained.

## EXPERIMENTAL

### Material

$\text{Ni}(\text{naph})_2$ ,  $\text{BF}_3\text{OEt}_2$ ,  $\text{Al}(\text{i-Bu})_3$  and butadiene are all polymerization reagent grade.  $\text{BF}_3\text{OEt}_2$

was dissolved in toluene (AR grade) or hydrogenated gasoline after it was distilled. Hydrogenated gasoline was repeatedly purified and then stored under high purity nitrogen. Butadiene was distilled for three times.

All samples were prepared and characterized in an inert atmosphere (high purity nitrogen) at room temperature.

In order to make a comparison of absorption spectra of all solutions of Ni(II) complexes, it is important to guarantee the concentration of Ni(II) equal to  $5.2 \times 10^{-2} M$  in all samples to be determined and to use high purity nitrogen to protect the samples from the damage by oxygen and trace of water.

## APPARATUS

Model 751G spectrometer (manufactured by Shanghai Analytical Instrument Factory) and HITACHI-304 spectrometer, and all the samples were in a 1-cm quartz cell.

## RESULTS AND DISCUSSIONS

### Binary system $Ni(naph)_2-Al(i-Bu)_3$

The UV-VIS spectra of butadiene and  $Ni(naph)_2$  in hydrogenated gasoline were determined respectively. The spectrum shown in Figure 1 reveals an intensive absorption band of butadiene at 218nm, extinction coefficient is about  $1.9 \times 10^4$ . Based on FEMO method, by the model of particle-in-a-box, it is well known that in butadiene,  $H_2C=CH=CH=CH_2$ , each carbon atom contributes one electron to the double bond system, and these four electrons probably can spread over the entire length of the chain. The energy states can be obtained from equation  $E = 1.12n^2$ , and the four electrons fill the first two lower levels as illustrated in Figure 2.

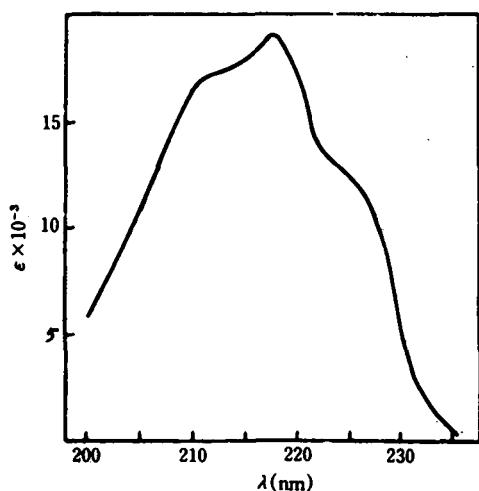


Fig.1 Absorption spectrum of butadiene in hydrogenated gasoline

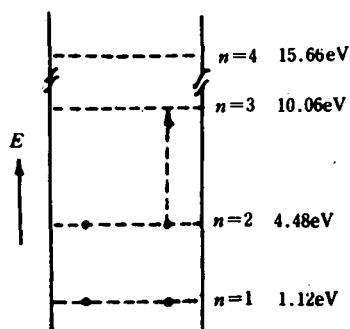


Fig. 2 Particle-in-a-box energy level scheme for butadiene

The first excited state of this system has one electron in the  $n = 3$  level, and the energy to produce this state corresponds to  $45,000 \text{ cm}^{-1}$ . Butadiene does have an absorption band at  $45870 \text{ cm}^{-1}$  ( $\lambda = 218 \text{ nm}$ ) as shown in Figure 1.

Ni(II) naphthenate in hydrogenated gasoline is light green, which is due to the presence of weak absorption bands in the red and blue region of the visible spectrum, the bands are

| $\lambda$                      | $\epsilon$ |
|--------------------------------|------------|
| 24800 $\text{cm}^{-1}$ (403nm) | 24.5       |
| 14700 $\text{cm}^{-1}$ (680nm) | 7.6        |
| 8550 $\text{cm}^{-1}$ (1170nm) | 8.1        |

If we compare the curve a (the lowest one) with the spectrum of  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$  (the upper curve c) in Figure 3<sup>[5,6]</sup>, it can be found that the three absorption bands of curves a and c are very similar. There is also a weak band in the region 680—900 nm on curve a, which may be attributed to spin-forbidden transitions. Three bands are related to the spin-allowed transitions from the  $^3A_{2g}$  ground state to the three excited triplet states. The problem is to obtain the right assignment of the bands. The obvious assignment is

|                                                    |        |                        |
|----------------------------------------------------|--------|------------------------|
| $^3T_{2g}(\text{F}) \leftarrow ^3A_{2g}(\text{F})$ | (10Dq) | 8550 $\text{cm}^{-1}$  |
| $^3T_{1g}(\text{F}) \leftarrow ^3A_{2g}(\text{F})$ |        | 14700 $\text{cm}^{-1}$ |
| $^3T_{1g}(\text{P}) \leftarrow ^3A_{2g}(\text{F})$ |        | 24800 $\text{cm}^{-1}$ |

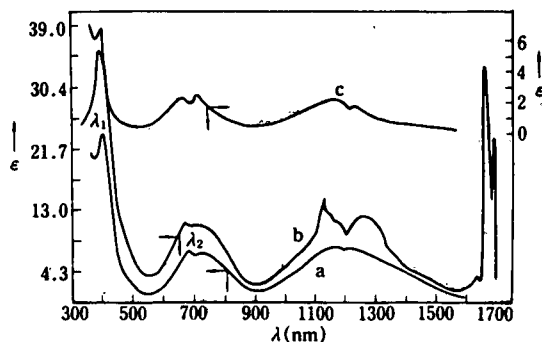
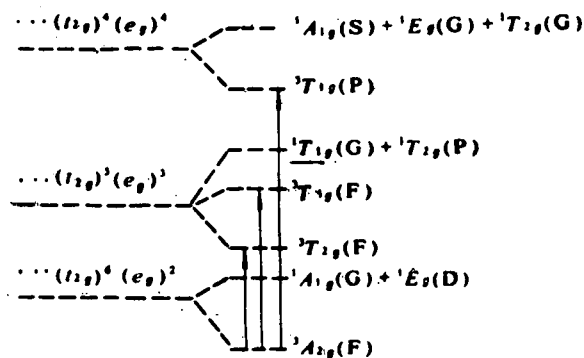


Fig. 3 Comparison of the spectra of  $\text{Ni}(\text{naph})_2$  (curve a),  $\text{Ni}(\text{naph})_2 + \text{BF}_3 \cdot \text{OEt}_2$  (curve b), and  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$  (curve c)

Based on the principle of ligand field theory, we can draw the state diagram of Ni(II) ( $d^8$ ) complexes as follows:



State diagram of  $d^8$  complexes

The ratio

$$\frac{{}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)}{{}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)} = 1.69$$

is used to fit the results of reference[6] because it is the most sensitive one. The required internal ratio is obtained for

$$|Dq/B| = 1.16$$

and the following can also be derived.

$$\frac{{}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)}{B} = 18.3 = 14700/B$$

Hence, for  $\text{Ni}(\text{naph})_2$ ,

$$B = 803 \text{ cm}^{-1}$$

$$10Dq = 9300 \text{ cm}^{-1}$$

Where  $B$  is referred to as a Racah parameter and is a sum of electron repulsion integrals.  $10Dq$  is the crystal field splitting parameter. The value of  $B$  for the free  $\text{Ni}^{+2}$  ion is  $1082 \text{ cm}^{-1}$ . There is a reduction to about 74% of the free-ion value for the interelectronic repulsion parameter upon incorporation of the ion into the complex, while  $B$  of  $\text{Ni}^{+2}$  in  $\text{Ni}(\text{naph})_2$  has a smaller value than that of  $\text{Ni}(\text{H}_2\text{O})^{+2}$ . This implies that (a) the metal electrons are partially delocalized and (b) the effective charge on the transition metal,  $\text{Ni(II)}$ , is smaller than that of the free ion. These effects shows that the metal electron cloud is more diffusive in the complex than in the free ion and electron repulsion therefore reduced.

On the other hand, the result of determination of magnetic susceptibility of  $\text{Ni}(\text{naph})_2$  in hydrogenated gasoline shows that the effective magnetic moment  $\mu_{eff}$  is 3.07 (at 298K)<sup>[7]</sup>. Based on the data mentioned above, we suggest that  $\text{Ni}(\text{naph})_2$  in hydrogenated gasoline or toluene is trimer with octahedral structure, which is similar to that of  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$ . It can be seen from Figure 4 that there are six oxygen atoms around the  $\text{Ni(II)}$  forming an octahedron, which may be irregular octahedron. That is due to the fact that, in the x-y plane, four bonds in  $\text{Ni-O}$  are equivalent but different from those in Z-direction, so that the symmetry of the complex reduces from  $O_h$  to  $D_{4h}$ .

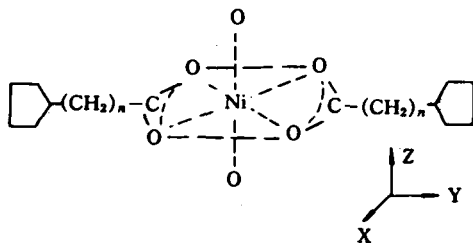


Fig. 4 Octahedral complex of  $\text{Ni}(\text{naph})_2$  in hydrogenated gasoline

Figure 5 shows UV-VIS spectra of binary system  $\text{Ni(naph)}_2\text{—C}_4\text{H}_6$  (butadiene). Two similar characteristic absorption curves (shown by a and b) of Ni(II) spin-allowed d-d transition at 403, and 680 nm, with molar ratio  $\text{C}_4\text{H}_6/\text{Ni(naph)}_2 = 63$  and 0.4, can be observed. This indicates no chemical reaction between  $\text{Ni(naph)}_2$  and  $\text{C}_4\text{H}_6$  at room temperature, which is in agreement with the studies of Tkáč and coworkers.

The determination of the magnetic susceptibility of  $\text{Ni(naph)}_2\text{—C}_4\text{H}_6$  system shows this system is paramagnetism<sup>[7]</sup> without interaction between them.

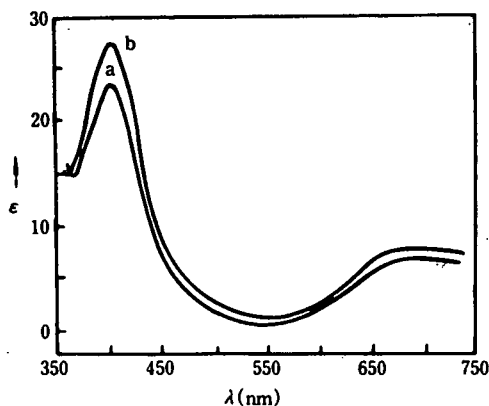


Fig. 5 Absorption spectra of  $\text{Ni(naph)}_2\text{—C}_4\text{H}_6$  in hydrogenated gasoline  
 $\text{C}_4\text{H}_6/\text{Ni(naph)}_2$ : a) 63; b) 0.4

#### Binary system $\text{Ni(naph)}_2\text{—BF}_3\text{·OEt}_2$

When the  $\text{Ni(naph)}_2$  is mixed with  $\text{BF}_3\text{·OEt}_2$ , the solution turns to yellow immediately for molar ratio  $\text{BF}_3\text{·OEt}_2/\text{Ni(naph)}_2 < 0.5$ , but for the ratio  $\geq 0.5$ , it appears dark yellow and precipitation occurs from solution.

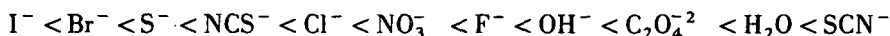
The UV-VIS spectrum of curve b in Figure 3 shows three new weak d-d bands appear in the region 360—1660 nm, at 395, 670, and 1137 nm. Near 1137 nm is a splitting of absorption band forming a new peak at 1240 nm. This reveals that the naphthenate ion is exchanged for halogen in the system to form a new Ni(II) complex called F-B-Ni complex. A comparison of the absorption spectra of the three Ni(II) complexes is compiled in Table 1.

Table 1 A comparison of the absorption spectra of Ni(II) complexes

| Ni(II) complexes                                  | The peak of absorption bands (nm) |             |             |             |
|---------------------------------------------------|-----------------------------------|-------------|-------------|-------------|
|                                                   | $\lambda_1$                       | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ |
| $\text{Ni(H}_2\text{O)}_6^{+2}$                   | 395                               | 689         | 1149        |             |
| $\text{Ni(naph)}_2$<br>(in hydrogenated gasoline) | 403                               | 680         | 1170        |             |
| 'F-B-Ni' complex<br>(in hydrogenated gasoline)    | 395                               | 670         | 1137        | 1240        |

From Figure 3 and Table 1, it can be seen that three bands of 'F-B-Ni' complex all shift to shorter wavelength site while the contour of curve b remains very analogous to those of other two complexes (the curve a and c in Figure 3), leading to the conclusion that the stereostructure of 'F-B-Ni' complex should be also octahedral.

On the other hand, according to the spectrochemical series of the complexes, the order of increasing "field strength" of some ligands is shown below.



The spectra data obtained from Figure 3 are not in agreement with the spectrochemical series. This problem is worthy of our further investigation in order to interpret the electronic spectrum of 'F-B-Ni' complex and to determine the number of fluorine atoms therein.

The magnetic susceptibility of binary system  $\text{Ni}(\text{naph})_2 \cdot \text{BF}_3 \cdot \text{OEt}_2$  shows that the 'F-B-Ni' complex is paramagnetism, and the oxidation state of Ni(II) in complex does not change.

#### Binary system $\text{Ni}(\text{naph})_2 \cdot \text{Al}(\text{i-Bu})_3$

UV-VIS spectra of samples for different molar ratios of  $\text{Ni}(\text{naph})_2/\text{Al}(\text{i-Bu})_3$  shown in Figure 6 indicate that with  $\text{Al}(\text{i-Bu})_3/\text{Ni}(\text{naph})_2 < 0.53$ , at 22°C, the characteristic absorption bands of

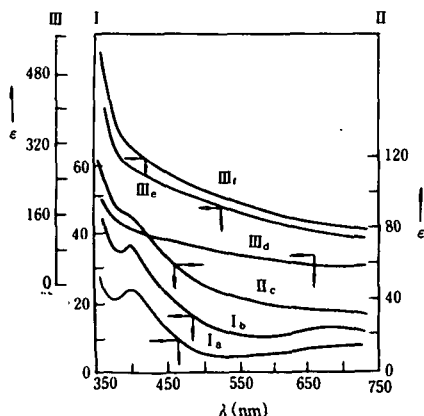
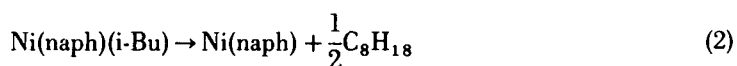
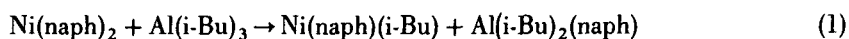


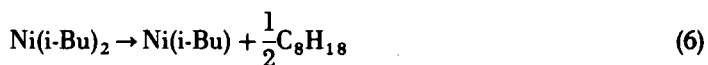
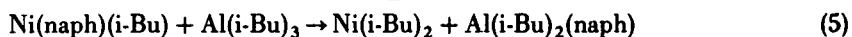
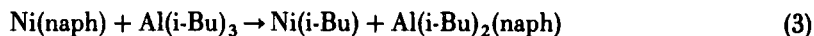
Fig. 6 Absorption spectra of  $\text{Ni}(\text{naph})_2 \cdot \text{Al}(\text{i-Bu})_3$  in hydrogenated gasoline

Molar ratios of  $\text{Ni}(\text{naph})_2/\text{Al}(\text{i-Bu})_3$ :

a) 0.20; b) 0.40; c) 0.53; d) 0.67; e) 1.6; f) 2.0; at 20–22°C

Ni(II) at 403 nm does not shift. When molar ratio equals or exceeds the value of 0.53, the color of the solution change from light green to dark black. The peaks at 403 nm turn out to be a shoulder-shape until disappearance. For  $\text{Al}(\text{i-Bu})_3/\text{Ni}(\text{naph})_2$  from 0.20 to 2.0, the naphthenate ion attached to Ni(II) can be exchanged for an alkyl group from triisobutylaluminium, and the Ni(II) is reduced to Ni(I) and Ni(0). The following chemical reactions may take place in the system





### Three-component system $\text{Ni(naph)}_2\text{-C}_4\text{H}_6\text{-Al(i-Bu)}_3$

Figure 7 clearly shows that the characteristic absorption bands of this system, with  $\text{Al(i-Bu)}_3/\text{Ni(naph)}_2 = 0.53$  and  $0.67$ , at  $403$  and  $680$  nm, all disappear. It indicates that  $\text{Ni(II)}$  is reduced to  $\text{Ni(I)}$  and  $\text{Ni(O)}$  due to the presence of butadiene under the small value of molar ratio. This result is in conformity with the result determined by magnetic susceptibility<sup>[7]</sup>. In our opinion the interaction between butadiene and  $\text{Ni(I)}$  or  $\text{Ni(O)}$  may take place to form two complexes<sup>[4]</sup>, the reaction may be formulated as follows:

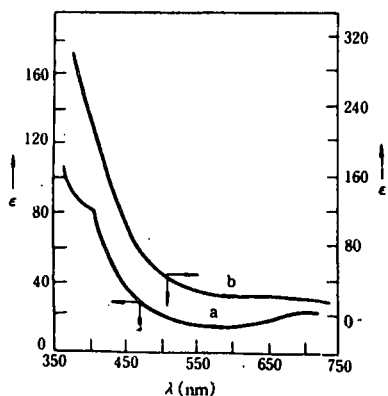
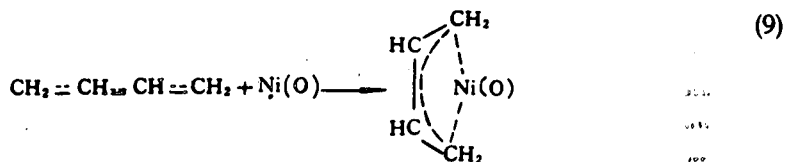
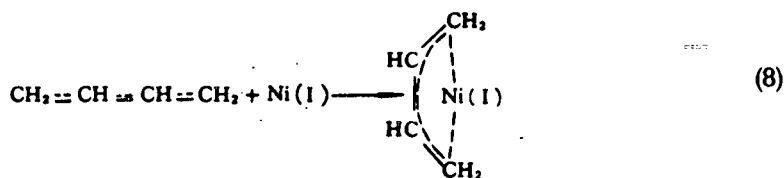


Fig.7 Absorption spectra of three-component system  $\text{Ni(naph)}_2\text{-C}_4\text{H}_6\text{-Al(i-Bu)}_3$   
 $\text{Al(i-Bu)}_3/\text{Ni(naph)}_2$ : a) 0.53; b) 0.67; at  $20\text{-}22^\circ\text{C}$

### Three-component system $\text{Ni(naph)}_2\text{-BF}_3\cdot\text{OEt}_2\text{-C}_4\text{H}_6$

Fig. 8 shows that the spectrum of this system is similar to that of  $\text{Ni(naph)}_2\text{-BF}_3\cdot\text{OEt}_2$  system, which exhibits the characteristic spectrum of 'F-B-Ni' complex not to be influenced by the presence of butadiene. In other words, no chemical reaction takes place between 'F-B-Ni' complex

and butadiene at room temperature.

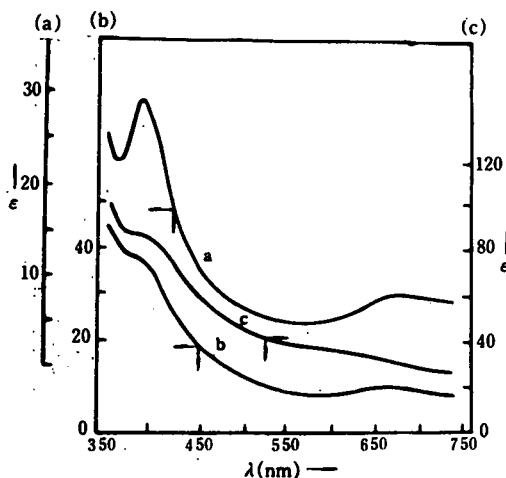


Fig 8 Absorption spectra of three-component system  $\text{Ni}(\text{naph})_2\text{-BF}_3\text{·OEt}_2\text{-C}_4\text{H}_6$  and  $\text{Ni}(\text{naph})_2\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$

| (a, curve)                                            | (b, c, curve)                                         |
|-------------------------------------------------------|-------------------------------------------------------|
| $\text{BF}_3\text{·OEt}_2/\text{Ni}(\text{naph})_2$ : | $\text{BF}_3\text{·OEt}_2/\text{Ni}(\text{naph})_2$ : |
| a 0.85;                                               | b 0.85; c 0.85;                                       |
| $\text{C}_4\text{H}_6/\text{Ni}(\text{naph})_2$ :     | $\text{Al}(\text{i-Bu})_3/\text{Ni}(\text{naph})_2$ : |
| a 3.0                                                 | b 0.4; c 0.67                                         |

### Three-component system $\text{Ni}(\text{naph})_2\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$

The absorption spectra of this system in Figure 8 show different pattern from those of  $\text{Ni}(\text{naph})_2\text{-Al}(\text{i-Bu})_3$  system (in Figure 6). The reason is the presence of  $\text{BF}_3\text{·OEt}_2$  and formation of 'F-B-Ni' complex.

We have also determined the magnetic susceptibility for  $\text{Ni}(\text{naph})_2\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$  system and  $\text{Ni}(\text{naph})_2\text{-C}_4\text{H}_6\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$  system. It has been found that Ni(II) is reduced to Ni(0) very rapidly due to the presence of the  $\text{BF}_3\text{·OEt}_2$  and formation of 'F-B-Ni' complex in  $\text{Ni}(\text{naph})_2\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$  system, and there is a competition of butadiene with  $\text{BF}_3\text{·OEt}_2$  for Ni(0) in  $\text{Ni}(\text{naph})_2\text{-C}_4\text{H}_6\text{-BF}_3\text{·OEt}_2\text{-Al}(\text{i-Bu})_3$  system.

### Keywords:

*cis*-1, 4-polybutadiene; Nickel catalyst; Ziegler-Natta catalyst; UV-VIS spectrum

### REFERENCES

- [1] Tkač, A., and Staško, A., *Collect, Czech. Chem. Comm.*, **1972**, 37, 573.
- [2] Tkač, A., and Staško, A., *Collect, Czech. Chem. Comm.*, **1972**, 37, 1006.
- [3] Tkač, A., and Staško, A., *Collect, Czech. Chem. Comm.*, **1972**, 37, 1295.
- [4] 华士英、唐学明, 高分子通讯 (*Polymer Communications*), **1982**(5), 331.
- [5] Harris, D.C., and Bertolucci, M.D., "Symmetry and Spectroscopy", New York, **1978**, p. 404, 405.
- [6] Figgis, B.N., "An Introduction to Ligand Field", John Wiley & Sons, New York, **1966**, pp.220, 169.
- [7] 陈滨宝、梁玉华、周治华、唐学明, 合成橡胶工业 (*Synthetic Rubber Industry*), **1985**, 8(5), 323.