

# COPOLYMERIZATION OF BUTADIENE AND ISOPRENE CATALYZED BY $V(acac)_3-Al(i-Bu)_2Cl-Al_2Et_3Cl_3$ CATALYST AND CHARACTERIZATION OF THE PRODUCTS\*

HU Zhenya (胡振亚), WEI Jinzhu (魏金柱), YANG Jipo (杨吉波) and LI Xiaoyan (李晓燕)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

## ABSTRACT

Copolymerization of butadiene and isoprene catalyzed by the catalyst system  $V(acac)_3-Al(i-Bu)_2Cl-Al_2Et_3Cl_3$  has been studied. Composition, microstructure, crystallinity and melting point of the copolymer obtained were determined by PGC, IR, X-ray diffraction and DSC methods respectively. The results revealed that the product was a copolymer and not a blend. The butadiene units presented in the copolymer were of *trans*-1,4-configuration, while the isoprene units were of both *trans*-1,4- and 3,4- forms. The melting point and crystallinity of the copolymer decreased with increase of molar ratio of isoprene to butadiene.

## INTRODUCTION

Copolymerization of butadiene and isoprene has been studied mostly with  $Co$ -<sup>[1-3]</sup>,  $Ti$ -<sup>[3,4]</sup> and  $Ln$ -<sup>[5-7]</sup> based catalysts with an attempt to modify certain properties of *cis*-1,4-polybutadiene. The application of vanadium catalyst in this case was rather rare, probably due to the fact that this catalyst system usually led the polymer to *trans*-configuration in the homopolymerization of butadiene, a product with a melting point of 145°C. However, this picture seemed to have changed since the discovery of the *trans*-(butadiene-piperylene) elastomer<sup>[8]</sup>. Our interest was to find any possibility of synthesizing crystallizable elastomer by breaking down the crystalline structure of *trans*-polybutadiene chain through insertion of isoprene units.

## EXPERIMENTAL

### Reagents

Butadiene (Bd) and Isoprene (Ip) were of solution polymerization grade, and the latter was stored over active alumina and redistilled before use. Toluene was of analytical grade, refluxed over  $LiAlH_4$  and redistilled before use.  $V(acac)_3$  and  $Al(i-Bu)_2Cl$  were prepared according to literature<sup>[9, 10]</sup> and diluted with toluene to a concentration of  $1.08 \times 10^{-5}$  mol/ml and  $5.07 \times 10^{-3}$  mol/ml respectively.  $Al_2Et_3Cl_3$  was a commercial product and was diluted

\* Received February 24, 1983

with toluene to a concentration of  $4 \times 10^{-4}$  mol/ml.

### Copolymerization

Copolymerization was carried out at constant temperature in glass ampoules having a volume of ca. 50 ml each, dried and purged with nitrogen thrice under heating before use. The order of reagents addition was: toluene solution of butadiene, isoprene,  $\text{Al}_2\text{Et}_3\text{Cl}_3$  and  $\text{Al}(i\text{-Bu})_2\text{Cl}$  solutions.  $\text{V}(\text{acac})_3$  solution was injected finally with a syringe after the ampoules in the thermostat reached the polymerization temperature. Unless stated otherwise, the general recipe used in this study was: monomer (butadiene and isoprene) concentration = 0.1 mol/25 ml;  $\text{Bd/Ip} = 30/70$ ;  $\text{V}(\text{acac})_3/\text{monomer} = 3 \times 10^{-4}$ ;  $\text{Al}(i\text{-Bu})_2\text{Cl}/\text{V}(\text{acac})_3 = 20$  and  $\text{Al}_2\text{Et}_3\text{Cl}_3/\text{V}(\text{acac})_3 = 5$ , all in molar ratio; the polymerization temperature was  $3^\circ\text{C}$  and the time of polymerization was 15 hours. The polymerization was terminated by adding ethyl alcohol containing 1% 2,6-di-*ter*-butyl-4-methyl-phenol and the product was washed with the same solvent and dried under vacuum below  $40^\circ\text{C}$ .

### Characterization

Intrinsic viscosity of the product was determined at  $30^\circ\text{C}$  by using Ubbelohde viscometer with toluene as the solvent, microstructure by Perkin-Elmer 599B infrared spectrometer, composition by  $^1\text{H-NMR}$  and Curie point pyrolytic gas chromatography (pyrolytic temperature,  $770^\circ\text{C}$ ; pyrolytic time, 1 sec). Chromatographic analysis conditions: column, 2 meters, 3 mm i.d. stainless steel tube, packed with 20% polymethylvinylsiloxane on 60/80 Chromosorb W, operated isothermally at  $90^\circ\text{C}$ ; carrier gas,  $\text{N}_2$ ; precolumn pressure,  $0.7 \text{ kg/cm}^2$ . Degree of crystallinity was determined by a Rigaku X-ray diffractometer,  $\text{CuK}_\alpha$  radiation with Ni filter, 35KV, 15mA.

## RESULTS AND DISCUSSION

### Identification of products

Homopolymerization of butadiene and copolymerization of butadiene and isoprene were carried out under conditions described in the experimental part. The infrared spectrum of the copolymerization product was shown in Fig. 1.

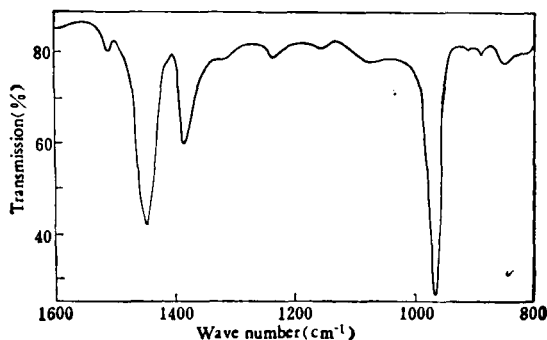


Fig. 1 Infrared spectrum of the copolymerization product of butadiene and isoprene with  $\text{V}(\text{acac})_3\text{-Al}(i\text{-Bu})_2\text{Cl-Al}_2\text{Et}_3\text{Cl}_3$  catalyst system

The strong absorption at  $967\text{cm}^{-1}$  indicates that its butadiene unit is essentially of *trans*-1,4 configuration, while its isoprene unit is partly of *trans*-1,4- (absorption at  $1150\text{ cm}^{-1}$ ) and partly of 3,4- configuration ( $888\text{ cm}^{-1}$ ).

Table 1 shows the solubility behavior of homopolymer of butadiene and its copolymer with isoprene in toluene at room temperature.

**Table 1** Solubility behavior of homopolymer of butadiene and its copolymerization product with isoprene in 30 ml toluene at  $18^\circ\text{C}$  after standing 15 hours

| Sample             | Content of <i>trans</i> -1,4-PBd (%) | Weight of sample (g) | Weight of insoluble portion (g) | Soluble portion (%) |
|--------------------|--------------------------------------|----------------------|---------------------------------|---------------------|
| Homopolymer        | 99.0                                 | 0.0490               | 0.0455                          | 7                   |
| Copolymer. product | 75.7                                 | 0.0515               | 0.0013                          | 97                  |

The fact that the copolymerization product having a *trans*-1,4-polybutadiene content as high as 75.7% was soluble in toluene at  $18^\circ\text{C}$  can be only explained by assuming that this copolymerization product is a copolymer and not a blend of homopolymers of butadiene and isoprene. Otherwise, the *trans*-1,4-polybutadiene portion would have separated out from the solution. The close isoprene content of the fractionated portions of the copolymerization product as shown in Table 2 supports this assumption.

**Table 2** Isoprene content of fractionated portions of a copolymerization product having Ip content of 18.2% and  $[\eta]_{\text{tol}}^{30^\circ\text{C}} = 1.1\text{ dl/g}$

| Fraction                                        | 1    | 2    | 3    | 4    |
|-------------------------------------------------|------|------|------|------|
| Ip content (%)                                  | 16.6 | 16.6 | 16.0 | 17.8 |
| $[\eta]_{\text{tol}}^{30^\circ\text{C}}$ (dl/g) | 2.4  | 1.4  | 1.1  | 0.7  |

Pyrolysis gas chromatography study of the copolymerization sample affords another piece of evidence for the above assumption. Chromatogram of the present copolymerization product is similar to that of butadiene-isoprene copolymer prepared with Ln-catalyst<sup>[7]</sup> and differs from that of blend of polybutadiene and polyisoprene (Fig. 2).

#### *Preparation of copolymers having various isoprene contents*

A series of copolymers having various isoprene contents was prepared by changing polymerization conditions. It was found monomer concentration,  $\text{Al}(i\text{-Bu})_2\text{Cl}/\text{V}(\text{acac})_3$  ratio, as well as polymerization temperature and time affected the yield and intrinsic viscosity of the copolymers prepared but not their isoprene content. However, effect of  $\text{Al}_2\text{Et}_3\text{Cl}_3/$

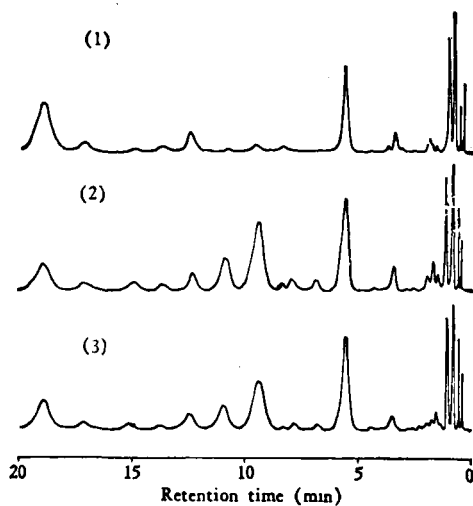


Fig. 2 The Pyrograms of polybutadiene-polyisoprene blend (curve 1), the present copolymerization product (Bd/Ip 63/37, curve 2) and copolymer of butadiene-isoprene prepared with Ln-catalyst (curve 3)

$V(acac)_3$  and monomer ratio on isoprene content was significant (Tables 3 and 4). One can see from Table 3 that copolymer with an isoprene content up to 43.5% was obtained at  $Al_2Et_3Cl_3/V(acac)_3=0$  in a rather low conversion. The optimum  $Al_2Et_3Cl_3/V(acac)_3$  ratio was around 5, where the isoprene content was 28.4% at a conversion of 41.0%.

Table 3 Effect of  $Al_2Et_3Cl_3/V(acac)_3$  on the conversion, intrinsic viscosity and isoprene content

| $Al_2Et_3Cl_3/V(acac)_3$<br>(mol/mol) | Conversion<br>(%) | $[\eta]_{tol}^{30^\circ C}$<br>(dl/g) | Ip content<br>(%) |
|---------------------------------------|-------------------|---------------------------------------|-------------------|
| 0                                     | 6.0               | 1.2                                   | 43.5              |
| 5                                     | 41.0              | 1.1                                   | 28.4              |
| 10                                    | 43.9              | 1.2                                   | 27.8              |
| 15                                    | 29.8              | 1.6                                   | 25.8              |
| 20                                    | 23.5              | 1.5                                   | 22.0              |

Polymerization conditions: Bd/Ip=30/70;  $V(acac)_3/M=3.0 \times 10^{-4}$ ;  $Al(i-Bu)_2Cl/V(acac)_3=20$ ; polymerization temperature, 30°C; 15 hrs.

Table 4 shows that the isoprene content of the copolymer increased with an increase in Ip/Bd ratio, but the higher the Ip/Bd ratio, the lower the conversion. No product was obtained in the case of pure isoprene. The most desirable Ip/Bd ratio lies in the range from 7/3 to 5/5.

**Table 4** Effect of monomer ratio on the conversion, intrinsic viscosity and isoprene content

| Ip/Bd<br>(mol/mol) | Conversion<br>(%) | $[\eta]_{\text{tol}}^{30^\circ\text{C}}$<br>(dl/g) | Ip content<br>(%) |
|--------------------|-------------------|----------------------------------------------------|-------------------|
| 10/0               | 0                 | —                                                  | —                 |
| 9/1                | 6                 | 0.2                                                | —                 |
| 8/2                | 13                | 0.5                                                | 36.7              |
| 7/3                | 41                | 1.1                                                | 28.4              |
| 5/5                | 41                | 1.3                                                | 19.0              |
| 3/7                | 53                | 0.7                                                | 11.8              |
| 2/8                | 60                | 1.6                                                | 2.7               |
| 0/10               | 87                | —                                                  | 0                 |

Polymerization conditions: same as in Table 3 except that  $\text{Al}_2\text{Et}_3\text{Cl}_3/\text{V}(\text{acac})_3$  being kept constant.

#### Crystallinity and melting point of copolymers

The degree of crystallinity of four copolymer samples was determined by wide-angle X-ray diffraction method. Table 5 shows the relationship between composition of copolymers and crystallinity. A decrease in crystallinity with the increase of isoprene content is obvious.

**Table 5** Isoprene content of copolymers and their degree of crystallinity

| Sample No.                  | 1    | 2    | 3    | 4    |
|-----------------------------|------|------|------|------|
| Ip content (%)              | 36.7 | 33.3 | 24.3 | 20.3 |
| Degree of crystallinity (%) | 12.5 | 16.0 | 18.6 | 19.9 |

**Table 6** Melting point of the copolymer with relation to its composition

| Isoprene content<br>(%) | Melting point<br>(°C) |
|-------------------------|-----------------------|
| 0                       | 145                   |
| 20.7                    | 79                    |
| 36.7                    | 68                    |

Table 6 lists the melting points of two copolymer samples measured with DSC and that of *trans*-polybutadiene. The melting point of *trans*-(butadiene-isoprene) polymer decreased with an increase in isoprene content.

In comparison with *trans*-(butadiene-piperylene) elastomer described by M. Bruzzone<sup>[8]</sup>,

melting points of the present copolymer is higher in the same comonomer content range, i.e., the effect of copolymerization with isoprene on cracking down the crystalline structure of *trans*-polybutadiene chains is less efficient than that of copolymerization with piperylene. The fact that present copolymer with 36.7% isoprene content has a melting point of 68°C and degree of crystallization of 12.5% reveals that long sequences of *trans*-butadiene units are still present. Their presence indicates that the addition to a butadiene chain end is much easier for butadiene molecule than for an isoprene molecule, and on the contrary, the addition to an isoprene chain end is much difficult for an isoprene than for butadiene. The reason is obvious if the steric hindrance of both their active center and the monomer is considered. This explanation is further supported by the fact that there was no product obtained in the homopolymerization of isoprene with the present catalyst system.

Present copolymer may find some application in the field of hot-melt adhesive.

#### REFERENCES

- [1] Pasquon, I., Porri, L., Zambelli, A. et Ciampelli, F., *Chim. et Ind.*, **1961**, *43*, 509.
- [2] Weber, H., Schleimer, B. und Winter, H., *Makromol. Chem.*, **1967**, *101*, 320.
- [3] Бреслер, Л. С., Долгопосок, Б. А., Колечкова, М. Ф. и Кропанева, Е. Н., *Высокомолек. Соед.*, **1963**, *5*, 357.
- [4] 古川淳二, 三枝武夫, 伊亮子光一, 広岡 昇, 成宮恒昭, 工业化学杂志(日), **1962**, *65*, 2074.
- [5] 中国科学院应用化学研究所四室, «稀土催化合成橡胶文集», 科学出版社, **1980**, 174.
- [6] 中国科学院应用化学研究所四室, «稀土催化合成橡胶文集», 科学出版社, **1980**, 16.
- [7] 沈之荃、宋襄玉、肖淑秀、杨吉坡、阙香兰, 中国科学, **1981**, 1341.
- [8] Bruzzone, M. and Carbonaro, A., *Rubber Chem. & Technol.*, **1978**, *51*, 907.
- [9] Morgan, G. T. and Moss, H. M., *J. Chem. Soc.*, **1913**, *10* (3), 78.
- [10] Bähr, G., Burßa, P., Lehmkuhl, H. und Ziegler, K., in Müller, E., "Methoden der Organischen Verbindungen", Band 13/4, George Thieme Verlag, Stuttgart, **1970**, 60.