# Conductivity of $I_2$-Doped High *trans*-1,4-Polybutadiene

SHI, Chen-Jun[a](史辰君) XUE, Huai-Guo[a](薛怀国) SHEN, Zhi-Quan*,[a](沈之荃)
ZHANG, Yi-Feng[a](张一烽) LI, Yong-Fang[b](李永舫) YANG, Chun-He[b](杨春和)
[a] *Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China*
[b] *Institute of Chemistry, Chinese Academy of Science, Beijing 100080, China*

**High *trans*-1,4-polybutadiene (~96% (*trans*)) was prepared by lanthanum naphthenate catalytic system. The conductivity of obtained polybutadiene doped with iodine reaches about ~$10^{-3}$ s/cm, which is 2 orders of magnitude higher than the value reported.[4,5] During the $I_2$-doping, the conjugated sequence was formed through double bond shifting reaction. According to the relationship between conductivity and temperature, conducting mechanism of doped high *trans*-1,4-polybutadiene is fit on variable range hoping (VRH) model.**

**Keywords** *trans*-1,4-Polybutadiene, $I_2$-doping, conductivity, hoping model

## Introduction

After Thakur[1] reported that conductivity of *cis*-1,4-polyisoprene could be increased by about 10 orders of magnitude upon "doping" with iodine, various other polydienes, such as *trans*-1,4-polyisoprene, 1,4-poly(2,3-dimethylbutadiene), and *trans*-1,4-polybutadiene, were found to be conductive when doped with iodine. All these observations generated considerable interest.[2,3] Shang *et al*. considered that the conductivity is raised from charge transfer complex formed by double bond and iodine cation.[4] However, Dai's studies[5,6] showed that the conductivity of polydienes comes from the conjugated sequence formed through double bond shifting reaction during $I_2$-doping.

Two kinds of conductivity of *trans*-1,4-polybutadiene (inclusion polymerization made one and 55% *trans*-1,4-polybutadiene) doped with iodine (~$10^{-5}$ s/cm) were reported.[4,5] In this paper, we report the conductivity (~$10^{-3}$ s/cm) of $I_2$-doping high *trans*-1,4-polybutadiene (~96% (*trans*)) synthesized by lanthanum naphthenate catalytic system. The influences of molecular weight of *trans*-1,4-polybutadiene and the measuring temperature on the conductivity were also studied.

## Experimental

### *Materials*

Butadiene and hydrogenated benzine were obtained from Shanghai Gaoqiao Chemical plant. Butadiene was purified by KOH and $\gamma$-$Al_2O_3$. *n*-Dibutyl magnesium containing 15% $AlEt_3$ was synthesized with method in literature.[7] All other chemicals are analytical grade reagents.

### *Synthesis and property of high trans-1,4-polybutadiene*

Polymerization of butadiene and preparation of catalyst solution were carried out in nitrogen and performed as described elsewhere.[8] The polymerization was terminated by adding ethanol containing 5% hydrochloric acid. The resulting polymer was washed by ethanol several times and dried to constant weight under vacuum at 40℃.

Table 1 lists the results of butadiene polymerization at various catalyst concentrations and the property of the high *trans*-1,4-polybutadiene prepared. The microstruc-

* E-mail: zqshen@163.net
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ture of polymer was determined with IR spectrophotometer (BRUKER). The intrinsic viscosity of the polymer obtained was determined by Ubbelohde viscometer in toluene at 30℃. The viscosity-average molecular weight was calculated according to the following equation:[9] $[\eta] = 2.94 \times 10^{-4} M_{\eta}^{0.753}$ (dL/g). The molecular weight distribution of polymer samples were narrow about 1.2, which was determined by GPC (waters 100, 25℃, THF as eluent).

**Table 1** Conditions of synthesis and physical property of polymer

| No. | Concentration of [La] (mol/L) | Conversion (%) | $M_{\eta}$ | Microstructure of polybutadiene | | |
|---|---|---|---|---|---|---|
| | | | | *trans*-1,4- (%) | *cis*-1,4- (%) | 1,2- (%) |
| 1 | $4.4 \times 10^{-3}$ | 96.0 | 6800 | 98 | ~0.1 | 2 |
| 2 | $3.1 \times 10^{-3}$ | 83.2 | 8400 | 97 | ~0.5 | 2 |
| 3 | $2.3 \times 10^{-3}$ | 72.6 | 10000 | 97 | ~0.6 | 2 |
| 4 | $1.8 \times 10^{-3}$ | 66.9 | 12000 | 97 | ~1 | 2 |

Polymerization conditions: La:$MgBu_2$:THF = 1:10:12 (molar ratio), [Bd] = 2.8 mol/L, solvent is hydrogenated benzine, 24 h, 50℃.

*$I_2$-Doping reaction*

A cyclohexane solution of 1.5 wt% high *trans*-1, 4-polybutadiene was coated onto glass plate, which was dried in vacuum 4 h. Then, 50—100 μm thick polybutadiene film was obtained. The *trans*-1,4-polybutadiene film was doped with iodine vapor at 30℃ according to the method in literature.[4] The iodine concentrations of the film were measured gravimetrically. The conductivity was measured by four-probe method at 20℃.

## Results and discussion

During the $I_2$-doping reaction, high *trans*-1, 4-polybutadiene film changed its color from white to brown, and at last became dark gray. With reaction progressing, iodine concentration of film became higher and higher until reaching saturation (Fig. 1). Saturated concentration of iodine was about 0.62—0.65 of iodine per butadiene unit. Thus the overdoped polymer can be represented as $[-(C_4H_6 \cdot I_y)-, y \approx 0.62]$.

Fig. 2 shows that the conductivity of high *trans*-1, 4-polybutadiene with saturated iodine ($y \approx 0.62$—0.65) reached about $10^{-3}$ s/cm. This value was 2 orders of magnitude higher than the values reported.[4,5]

Molecular weight of polymer usually affected its property. The relationship between conductivity of doped high *trans*-1, 4-polybutadiene and molecular weight is shown in Table 2. The data illustrate that the conductivities of samples with different molecular weights are in the same order of magnitude.

Temperature has great effect on conductivity of material and different matters follow different rules. The

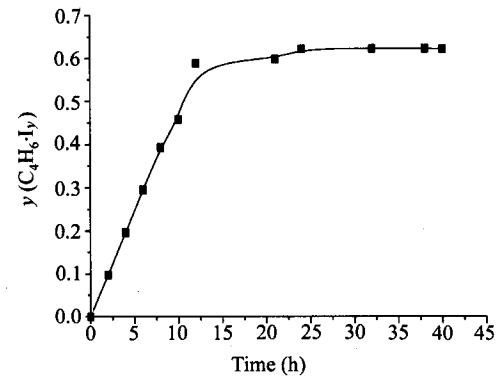


**Fig. 1** $I_2$ contents in doped high *trans*-polybutadiene as a function of doping time.

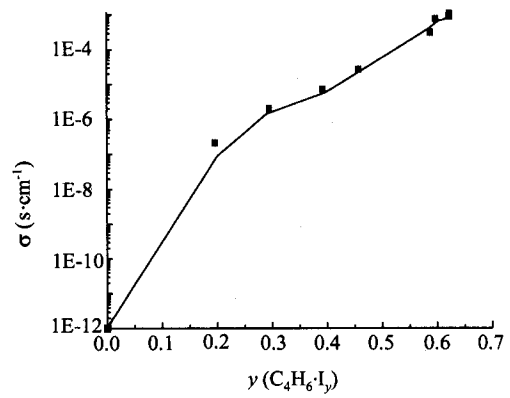


**Fig. 2** Electrical conductivities doped high *trans*-polybutadiene as a function of molar concentration ($y$) of iodine.

conductivity of $I_2$-doped high *trans*-1, 4-polybutadiene became higher when temperature raised as shown in Fig. 3. The ln σ has a linear relationship with $1/T^{1/4}$. This result was fit on Mott's VRH (variable range hopping) model.[10] It indicates that the conduction in this system adopts hopping processes.[11]

**Table 2** Relationship between molecular weight and conductivity

| No. | Thickness of film ($\mu$m) | $y$ ($C_4H_6 \cdot I_y$) | Molecular weight ($M_\eta$) | $\sigma$ (s/cm) |
|---|---|---|---|---|
| 1 | 89 | 0.62 | 6800 | $9.4 \times 10^{-4}$ |
| 2 | 54 | 0.64 | 8400 | $9.4 \times 10^{-4}$ |
| 3 | 84 | 0.65 | 10000 | $9.9 \times 10^{-4}$ |
| 4 | 57 | 0.62 | 12000 | $1.1 \times 10^{-3}$ |

Condition: The doping reaction had been conducted at 30℃ for 24 h. The conductivity was measured with four-probe method at 20℃.

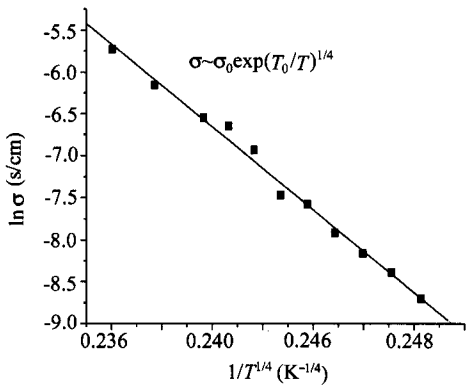


**Fig. 3** Relationship between conductivity and measuring temperature.

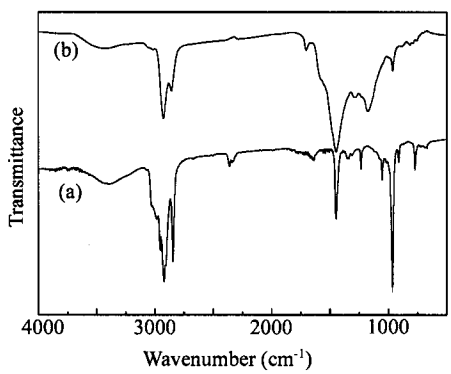


**Fig. 4** FTIR spectra of *trans*-polybutadiene before and after $I_2$-doping (a) spectrum of pristine polymer, (b) spectrum of polymer after $I_2$-doping.

Fig. 4 shows the FTIR spectra of the high *trans*-1, 4-polybutadiene film before and after $I_2$-doped. The IR spectrum of $I_2$-doped poly-1, 4-butadiene shows that the band of 960 $cm^{-1}$, which is characteristic of *trans* = CH out of plane (bending), and the band of 1650 $cm^{-1}$, which associated with stretching vibration of isolated C = C bonds, decreased in intensity. The bands in the range of 800—1350 $cm^{-1}$ increased considerably in intensity and broadened, leading a spectrum very similar to that of doped *cis*-1, 4-polyisoprene reported by Dai.[12] The band at 960 $cm^{-1}$ decreased in intensity with respect to the $-CH_2-$ deformation vibration at 1445 $cm^{-1}$. These changes in the FTIR spectra are consistent with the addition of iodine to C = C bonds along the polybutadiene backbones.[4] In addition, in Fig. 4(b), a broad band appeared at about 1590 $cm^{-1}$ consistent with the stretching mode of conjugated C = C bonds.[12] This may indicate the conjugated sequence of *trans*-1, 4-polybutadiene was formed during $I_2$-doping.[5,6]

Treatment of doped sample with $NH_3$ resulted in a reduction of the conductivity to pristine level. By redoping the above sample with iodine, the conductivity can restore to origin value ($\sim 10^{-3}$ s/cm). This shows that doping reaction is a reversible reaction.

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