



## Bromination of butyl rubber in rotating packed bed reactor

Wei Wang<sup>a,b</sup>, Hai-Kui Zou<sup>b,\*</sup>, Guang-Wen Chu<sup>a,b</sup>, Zhan Weng<sup>b</sup>, Jian-Feng Chen<sup>a,b,\*</sup><sup>a</sup> State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China<sup>b</sup> Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, PR China

## HIGHLIGHTS

- An RPB reactor was employed to intensify the bromination process of IIR.
- The time required to obtain high-quality BIIR was reduced to 1–2 min.
- Effects of bromination parameters were comprehensively studied.
- The potential of the RPB as an industrial bromination reactor was discussed.

## ARTICLE INFO

## Article history:

Received 25 July 2013

Received in revised form 24 October 2013

Accepted 29 October 2013

Available online 7 November 2013

## Keywords:

Butyl rubber

Bromination reactor

Rotating packed bed

Bromination parameters

## ABSTRACT

Bromination of butyl rubber (isobutylene isoprene rubber, IIR) in a conventional stirred tank reactor suffers from low efficiency and low quality due to slow micro-mixing. This study reports bromination of IIR in a rotating packed bed (RPB) with intensified micro-mixing. By varying bromination parameters, such as reaction time, reactant concentration, temperature and high-gravity level ( $G$ ), effects of these parameters on product quality in terms of the Br content ( $X_{Br}$ ) and the unsaturated degree ( $\Omega$ ) were investigated. Bromobutyl rubber (BIIR) with  $X_{Br}$  of 1.84–1.92 wt% and  $\Omega$  of more than 1.54 mol% was produced at an optimum range of  $G$ , 68–80 g. The time required to complete bromination was significantly reduced to 1.0–2.0 min (c.f. about hours in traditional industrial reactor). The results indicate that both high production efficiency and high quality of BIIR can be achieved in the RPB, which provides a new pathway for the industrial bromination process of IIR.

© 2013 Elsevier B.V. All rights reserved.

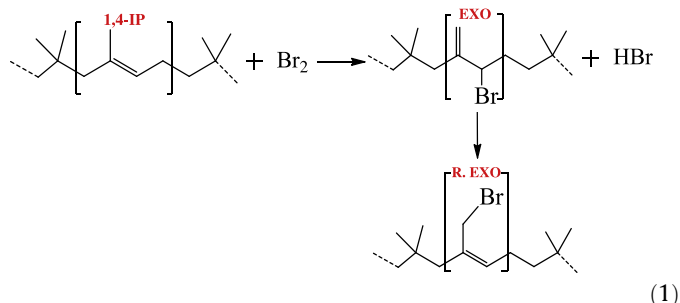
## 1. Introduction

Butyl rubber (isobutylene isoprene rubber, IIR) is a copolymer of isobutylene and isoprene. Bromobutyl rubber (BIIR) is a halogenated IIR that has been widely used in tires, inner tubes, tire inner liners, and rubber tire-curing bladders [1–3]. BIIR retains many of the desirable characteristics of IIR, such as low gas permeability, thermal and oxidative stability, and strong chemical resistance, while exhibits better performance on blending and vulcanizing in comparison with IIR [4–6]. BIIR can be synthesized via bromination of IIR in solution or in the extrusion process of dried IIR [7,8]. Bromination in solution is more widely adopted in the industrial production, because BIIR produced by the solution process is more stable and homogeneous than that produced by the extrusion process [2,7].

\* Corresponding authors. Address: State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China. Tel.: +86 10 64446466; fax: +86 10 64434784 (J.-F. Chen). Tel.: +86 10 64443134 (H.-K. Zou).

E-mail addresses: [zouhk@mail.buct.edu.cn](mailto:zouhk@mail.buct.edu.cn) (H.-K. Zou), [chenjf@mail.buct.edu.cn](mailto:chenjf@mail.buct.edu.cn) (J.-F. Chen).

The bromination of IIR in solution is mainly a substitution reaction rather than an addition reaction, and the main reaction is shown as:



where 1,4-IP is 1,4-isoprene unit in IIR, and EXO is an exo-allylic bromide structure (the main unit with Br in the product) [9–11]. A portion of EXO can be transferred to rearranged exo-allylic structure (R.EXO). The byproduct of the substitution reaction, HBr, can lead to hydro-bromination of 1,4-IP as shown below:

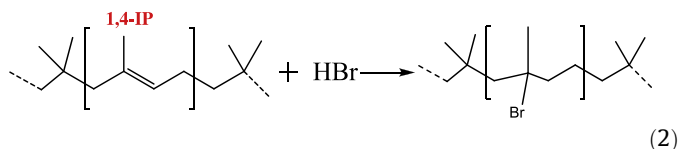
### Nomenclature

1,4-IP	1,4-isoprene unit in IIR and BIIR
$A_{\delta}$	integral area of characteristic peaks $\delta$
BIIR	bromobutyl rubber, brominated isobutylene isoprene rubber
EXO	exo-allylic bromide structure in BIIR
$G$	high-gravity level in RPB, g
$g$	acceleration of gravity = $10 \text{ m s}^{-2}$
IIR	butyl rubber, isobutylene isoprene rubber
$M$	atomic weight or molecular weight
RPB	rotating packed bed
R.EXO	rearranged exo-allylic structure in BIIR
$r$	geometric average radius of the packing, m
STR	stirred tank reactor
$t = t_0 + t'$	total reaction time of the bromination, min
$t_0$	reaction time of the bromination in RPB, min
$t'$	reaction time of the bromination in brown beakers, min

$T$	reaction temperature, $^{\circ}\text{C}$
$[1,4\text{-IP}]_0$	initial concentration of 1,4-IP in RPB, $\text{mmol L}^{-1}$
$[\text{Br}_2]_0$	initial concentration of $\text{Br}_2$ in RPB, $\text{mmol L}^{-1}$
$[\text{NaClO}]_0$	initial concentration of NaClO in RPB, $\text{mmol L}^{-1}$
$[\text{NaClO}]_0/[\text{Br}_2]_0$	initial concentration ratio of NaClO to $\text{Br}_2$
$X_{\text{Br}}$	content of bromine in the EXO structure and R.EXO structure in BIIR, wt%

### Greek symbols

$\Omega$	unsaturated degree (content of C=C bonds in IIR and BIIR), mol%
$\omega$	angular speed of the rotator, $\text{rad s}^{-1}$
$\varphi_{(\text{CH}_2\text{Cl}_2)}$	volume content of $\text{CH}_2\text{Cl}_2$ in the solvent, %
$\delta$	characteristic peaks in $^1\text{H-NMR}$ spectra of the product samples = 1.11, 4.05, 4.09, 4.34, 5.02, 5.07, 5.40 ppm



This is a side reaction which is the main cause of (1) the generation of saturated polymer, (2) the decrease in the C=C bonds content (i.e. unsaturated degree,  $\Omega$ ) in BIIR, and (3) not more than 50% of the utilization of bromine [2,3,9]. An effective measure to inhibit the negative effects of hydro-bromination has been proposed by Baade et al. [3,9]. By using mild oxidizing agents, such as NaClO solution with low concentration, HBr is converted back to  $\text{Br}_2$  without oxidizing the polymer. Further study [9] showed that a remarkable acceleration of the rate of reaction (1) was achieved with the use of an electrophilic reagent,  $\text{CH}_2\text{Cl}_2$ , as co-solvent, and the required reaction time can be reduced to 1.0–4.0 min in a 500 mL stirred tank reactor (STR) in laboratory. These results indicate that bromination of IIR is a rapid reaction in the presence of electrophilic solvent and oxidizing agent, and such a reaction process will be influenced by micro-mixing [12–15]. As a conventional choice of bromination reactor, STR is generally used in previous studies and industrial productions [9,16]. However, the conventional industrial STR has low micro-mixing efficiency and limits the reaction rate of bromination. This usually leads to hours of required reaction time in the industrial bromination process [16], and thus affects production efficiency and product uniformity. Therefore, a novel bromination reactor with high intensity and efficiency of micro-mixing is desired.

Rotating packed bed (RPB) is an apparatus creating a high-gravity environment via the action of centrifugal force. When passing through the packing of the RPB, liquid is accelerated and split into fine droplets, threads, and thin films by the rotating packing, resulting in significant intensification of micro-mixing and mass transfer [13,17–20]. The RPB also has the advantages of smaller equipment size and negligible scale-up effects compared to the conventional reactors [13–15,21]. Therefore, the RPB has been successfully adopted in the processes of reactive crystallization [22–28], distillation [29–31], and absorption [30,32–34]. The RPB has also been used to synthesize IIR by cationic polymerization and exhibited prominent characteristics of process intensification in organic synthesis [15].

In this study, an RPB was employed as the bromination reactor of IIR for the first time. The effects of bromination parameters, such

as reaction time, volume content ( $\varphi_{(\text{CH}_2\text{Cl}_2)}$ ) of the electrophilic co-solvent ( $\text{CH}_2\text{Cl}_2$ ) in the solvent, dosage of  $\text{Br}_2$ , dosage of the oxidant (NaClO), temperature ( $T$ ), and high-gravity level ( $G$ ) in the RPB, were studied. It was also attempted to determine the suitable process conditions for the production of BIIR with high Br content ( $X_{\text{Br}}$ ) and  $\Omega$ .

## 2. Experimental section

### 2.1. Materials and reagents

IIR532 with 1,4-IP content of 1.67 mol% ( $\Omega$  of the IIR) was purchased from Zhejiang Cenway New Materials Co. Ltd., (China), and bromine (purity  $\geq 99.5\%$ ) was purchased from Sinopharm Chemical Reagent Co. Ltd., (China). Hexane (purity  $> 95.0\%$ , Beijing Chemical Works, China), dichloromethane (purity  $> 95.0\%$ , Beijing Chemical Works, China), sodium hypochlorite solution (available chlorine content  $\geq 10\%$ , Tianjin Guangfu Chemical Research Institute, China), sodium hydroxide (purity  $> 95.0\%$ , Beijing Chemical Works, China) and chloroform-D (99.8%D + 0.03% v/v TMS, Qingdao Tenglong Weibo Technology Co. Ltd., China) were used in this work.

### 2.2. Experimental procedures

The schematic diagram of the experimental set-up for the synthesis of BIIR in the RPB has been shown in Fig. 1, and the RPB reactor has been shown in Fig. 2. The inner diameter and outer diameter of the packing in the RPB were 50 mm and 150 mm respectively, and the axial height of the packing was 53 mm. Bromine was dissolved in hexane and stored in tank 1. IIR was dissolved in a solvent comprised of hexane and  $\text{CH}_2\text{Cl}_2$ , and  $\varphi_{(\text{CH}_2\text{Cl}_2)}$  was regulated from 0% to 50%. The IIR solution with the addition of NaClO solution was stored in tank 2. The prepared solutions in tank 1 and 2 were pumped into RPB respectively with a volumetric flow rate ratio of 1:10. They met in the distributor (3 in Fig. 2) and jetted onto the inner edge of the rotator (4 in Fig. 2), followed by flowing through the packing and exiting the RPB. The initial concentrations of reactants in the RPB, including  $[1,4\text{-IP}]_0$ ,  $[\text{Br}_2]_0$  and  $[\text{NaClO}]_0/[\text{Br}_2]_0$ , were controlled at  $20 \text{ mmol L}^{-1}$ ,  $8\text{--}13 \text{ mmol L}^{-1}$  and 0–4 respectively by regulating their concentrations in the tanks [9]. The residence time of reactants in the RPB ( $t_0$ ), which is also the bromination time in the RPB, was less than  $1.67 \times 10^{-2}$  min (1 s) [30]. The solution from the RPB was then led into a neu-

Download English Version:

<https://daneshyari.com/en/article/147722>

Download Persian Version:

<https://daneshyari.com/article/147722>

[Daneshyari.com](https://daneshyari.com)