# Catalysis Science & Technology

# PAPER

Cite this: Catal. Sci. Technol., 2014, 4, 773

# Solvent effect on *cis*-1,4-specific polymerization of 1,3-butadiene with CoCl<sub>2</sub>(PRPh<sub>2</sub>)<sub>2</sub>-EASC catalytic systems

Qinzhuo Zhou, Bo-Geng Li, Suyun Jie\* and Na Zheng

A series of phosphine-containing cobalt complexes  $[CoCl_2(PRPh_2)_2, R = Ph (1), Cy (2), ^Pr (3), Et (4), Me (5), H (6)]$  has been used for the highly active and stereospecific polymerization of 1,3-butadiene upon activation with ethylaluminum sesquichloride (EASC). The high catalytic activities and polybutadienes with high *cis*-1,4 selectivity were obtained in the solution polymerization in toluene. The conversion of butadiene and the microstructure and molecular weight of the resulting polymers were affected by reaction parameters and the R group on the phosphine ligand. The dispersion medium was also a sensitive factor for the current catalytic systems, influencing the catalytic activity and properties of products. In comparison with the solution polymerization in toluene, the heterogeneous polymerization in isooctane yielded slightly lower catalytic activity, *cis*-1,4 content and molecular weight under similar reaction conditions.

Received 26th August 2013, Accepted 16th December 2013

DOI: 10.1039/c3cy00634d

www.rsc.org/catalysis

## Introduction

Polybutadienes (PBDs) are formed via 1,4- or 1,2-insertions, which lead to cis-1,4, trans-1,4 or 1,2-vinyl microstructures. In particular, selective cis-1,4-specific polymerization has attracted much attention, because the resulting cis-1,4-PBDs are the most important elastomers used for tires and other elastic materials.<sup>1,2</sup> The TiCl<sub>4</sub> or TiCl<sub>3</sub>-AlR<sub>3</sub> catalytic systems were firstly used in butadiene polymerization,<sup>3</sup> just after their application in the polymerization of ethylene and propylene. For an industrial scale, cis-1,4-PBDs are produced commercially via solution polymerization of 1,3-butadiene catalyzed by Ziegler-Natta catalysts, such as TiCl<sub>4</sub>-I<sub>2</sub>-Al(i-Bu)<sub>3</sub>,<sup>4</sup> CoCl<sub>2</sub>-AlEt<sub>2</sub>Cl,<sup>5,6</sup> Ni(OOCR)<sub>2</sub>-BF<sub>3</sub>·OEt<sub>2</sub>-AlEt<sub>3</sub>,<sup>7,8</sup> or Nd(OOCR)<sub>3</sub>-Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-Al(i-Bu)<sub>2</sub>H (ref. 9), in aromatic or aliphatic hydrocarbon solvents. Among those catalysts, the cobalt-based catalysts are of great importance in butadiene polymerization and have been widely investigated probably because they can produce PBDs with different microstructures, including cis-1,4-PBDs and syndiotactic 1,2-PBDs. The halides and carboxylates of cobalt are stereoselective to high cis-1,4-PBDs when activated with methylaluminoxane (MAO) or modified MAO (MMAO).<sup>10-15</sup> However, the addition of phosphines to certain Co-based catalytic systems could alter the regio- and/or stereospecificity of the active species from cis-1,4-specific to syndiotactic 1,2-specific.<sup>15-28</sup> Besides,

the type and amount of cocatalysts also have a great influence on catalytic activity and stereoselectivity of the resulting polymers.<sup>29–32</sup> In our previous study, the addition of triphenylphosphine to the [Co]–EASC catalytic systems didn't change the polymer microstructure.<sup>31</sup>

Heterogeneous polymerization is widely applied on an industrial scale because of the low viscosity of the polymer solution, easy dissipation of heat and temperature control, milder reaction conditions, product homogeneity, etc. 33,34 The cobalt allyl complex [Co(C<sub>8</sub>H<sub>13</sub>)(C<sub>4</sub>H<sub>6</sub>)] (ref. 35, 36) in combination with CS<sub>2</sub> for the catalytic polymerization of 1,3-butadiene afforded syndiotactic 1,2-PBDs with high 1,2-vinyl selectivity in aqueous emulsion.<sup>37-40</sup> The suspension polymerization of butadiene in the presence of titanium-magnesium nanocatalysts combined with Al(i-Bu)<sub>3</sub> yielded PBDs containing up to 99% trans-1,4-units.41 The cationic nickel(II) complexes were reported to catalyze butadiene polymerization in disperse aqueous systems with nonaqueous prepolymerization and special precautions to prevent the precatalyst from decomposing prematurely, producing PBDs with low monomer conversion and *cis*-1,4 content.<sup>42,43</sup> Furthermore, water is a toxic agent that makes catalysts inactive and causes danger in the process of olefin polymerization. Therefore, a nonaqueous solvent as the continuous phase is important in the heterogeneous polymerization of butadiene. The hydrocarbon mixtures (comprising a volume fraction greater than 80% of C4 hydrocarbons) were reported to be used as a dispersion medium for the production of *cis*-1,4-PBDs in suspension polymerization, where the polymerization was initiated by a rare earth compound;44 however, the catalytic activities were low and residual

COYAL SOCIETY OF CHEMISTRY

**View Article Online** 

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: jiesy@zju.edu.cn; Fax: +86 (0)571 87951612; Tel: +86 (0)571 87951515

Nd concentrations in the polymers were high (180–250 ppm).<sup>45</sup> Thus, a highly active and stereospecific catalytic system and a proper dispersion medium are necessary for the production of *cis*-1,4-PBDs in the heterogeneous polymerization of 1,3-butadiene.

In order to deeply explore the phosphine-containing cobalt-based catalytic systems and obtain high *cis*-1,4-PBDs, a series of phosphine-containing cobalt complexes  $[CoCl_2(PRPh_2)_2]$  has been investigated with EASC as the cocatalyst in the polymerization of 1,3-butadiene in different solvents. The effect of solvents, one aromatic (toluene) hydrocarbon, one aliphatic (isooctane) hydrocarbon and their mixture, on the catalytic activity, the microstructure and molecular weight characteristics of polybutadienes will be discussed in this paper.

## Results and discussion

### Polymerization of butadiene in toluene

The  $CoCl_2(PRPh_2)_2$ -MAO systems were reported to be extremely active in the polymerization of butadiene, producing 1,2-PBDs (70–88%) essentially, and the stereoregularity of products was affected by the bulkiness of the R group on the phosphorous atom.<sup>46</sup> In order to gain high *cis*-1,4-PBDs, ethylaluminum sesquichloride (EASC) was employed as the cocatalyst for  $CoCl_2(PRPh_2)_2$  [R = Ph (1), Cy (2), <sup>n</sup>Pr (3), Et (4), Me (5), H (6)] because it has been proven to be the more effective cocatalyst for the cobalt complexes in the polymerization of butadiene.<sup>29–32,47–49</sup> Hence, the solution polymerization of butadiene catalyzed by the  $CoCl_2(PPh_3)_2$  (1)-EASC catalytic system in toluene was investigated in detail under various reaction conditions to optimize the polymerization parameters, such as monomer concentration, Al/Co molar ratio, and reaction temperature (Table 1).

As the butadiene concentration increased, the reaction solution became more viscous; however, the conversion of butadiene to polymers wasn't affected and the complete conversions of butadiene were obtained for all the cases studied (entries 1–3 in Table 1). All the polymers obtained with different monomer concentrations were predominantly *cis*-1,4 isomers and the higher butadiene concentration resulted in the slight increase in *cis*-1,4 content from 96.2% to 97.1%. A similar trend was also observed in the polymerization of butadiene with the Co(acac)<sub>3</sub>–MAO system.<sup>10</sup> The molecular weight of PBDs increased gradually along with the increase in the Bd/Co molar ratio, while the molecular weight distribution didn't change greatly.

In the binary catalytic systems, it is known that the amount of cocatalyst has a great influence on the catalytic performance of precatalysts. However, the variation of the Al/Co molar ratio slightly affected the conversion of butadiene in the current systems and the high catalytic activities were obtained under a broad range of Al/Co molar ratio (entries 1 and 4–6 in Table 1). The butadiene conversion reached up to 96.5% even in the small amount of EASC (Al/Co = 20) and the 100% conversions of butadiene were obtained under the Al/Co molar ratio of both 40 and 80. The further increase in the

Table 1	Polymerization of 1,3-butadiene with $CoCl_2(PRPh_2)_2$ (1–6)–EASC in toluene <sup><math>a</math></sup>										
Entry	Cat.	Bd/Co	Al/Co	<i>T</i> (°C)	<i>t</i> (min)	Conv. (%)	$M_{\rm n}^{\ b} \ (10^4 {\rm \ g \ mol}^{-1})$	$M_{ m w}/M_{ m n}^{\ b}$	Microstructure <sup>c</sup> (mol%)		
									cis-1,4-	trans-1,4-	1,2-
1	1	2000	80	25	60	100	9.80	2.61	96.2	1.8	2.0
2	1	3000	80	25	60	100	17.6	2.97	96.9	1.6	1.5
3	1	4000	80	25	60	99.4	26.3	2.82	97.1	1.4	1.5
4	1	2000	20	25	60	96.5	12.3	2.75	96.8	1.5	1.7
5	1	2000	40	25	60	100	9.45	2.39	95.8	2.1	2.1
6	1	2000	160	25	60	97.8	11.5	3.10	97.0	1.3	1.7
7	1	2000	40	0	60	22.4	$30.1, 1.43^d$	$1.40, 1.63^d$	97.0	1.3	1.7
8	1	2000	40	50	60	98.8	4.28	2.73	88.3	6.8	4.9
9	1	2000	40	70	60	96.1	3.80	2.70	83.5	10.4	6.1
10	1	2000	40	90	60	96.3	3.46	3.27	78.8	15.6	5.6
11	2	2000	40	25	60	100	11.3	2.74	95.9	1.9	2.2
12	3	2000	40	25	60	100	8.69	2.72	96.1	2.0	1.9
13	4	2000	40	25	60	100	7.82	2.63	95.7	2.1	2.2
14	5	2000	40	25	60	100	7.83	2.71	96.0	1.8	2.2
15	6	2000	40	25	60	92.0	5.25	2.70	94.9	1.5	3.6
16	1	2000	40	25	10	51.7	14.8	1.57	97.2	1.2	1.6
17	2	2000	40	25	10	62.7	14.3	1.55	96.2	1.6	2.2
18	3	2000	40	25	10	63.9	13.6	1.53	96.7	1.4	1.9
19	4	2000	40	25	10	58.7	15.3	1.49	96.7	1.6	1.7
20	5	2000	40	25	10	53.9	14.0	1.52	97.0	1.4	1.6
21	6	2000	40	25	10	29.0	8.90	1.61	96.1	0.9	3.0
22	CoCl <sub>2</sub>	2000	40	25	60	Trace	_	_	_	_	_
$23^e$	CoCl <sub>2</sub>	2000	40	25	60	2.8	$41.9, 2.28^{f}$	$1.35, 1.80^{f}$	94.4	1.8	3.8

<sup>*a*</sup> Polymerization conditions: cat.: 5 µmol; cocat.: EASC; solvent: toluene, total volume: 15 mL. <sup>*b*</sup> Determined by GPC against polystyrene standards and reported uncorrected. <sup>*c*</sup> Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. <sup>*d*</sup> Bimodal distribution:  $30.1 \times 10^4$  g mol<sup>-1</sup> section occupied 81.2%,  $1.43 \times 10^4$  g mol<sup>-1</sup> section occupied 18.8%. <sup>*e*</sup> 10 µmol of CoCl<sub>2</sub>. <sup>*f*</sup> Bimodal distribution:  $41.9 \times 10^4$  g mol<sup>-1</sup> section occupied 45.6%,  $2.28 \times 10^4$  g mol<sup>-1</sup> section occupied 54.4%.

Al/Co molar ratio to 160 led to a slight decrease in butadiene conversion (97.8%). In the polymerization of olefins catalyzed by transition metal catalysts, the chain transfer to aluminum is usually an important factor to decrease the molecular weight of products, whereas its influence on the polymerization of butadiene didn't show good regularity. In addition, the variation of Al/Co molar ratio led to a slight change of the microstructure of PBDs.

The solution polymerization of butadiene was also carried out over the temperature range 0 to 90 °C with the 1-EASC catalytic system (entries 5 and 7-10 in Table 1). Although a lower conversion of butadiene (22.4%) was gained at 0 °C, some cobalt-based catalytic systems gave almost no activity under similar conditions.<sup>30,31</sup> The highest activity was observed at 25 °C with a complete conversion of butadiene. As the polymerization temperature was elevated, the conversion of butadiene decreased slightly, which demonstrated that the 1-EASC catalytic system has remarkable thermal stability at higher temperatures. At the same time, a lower molecular weight and a relatively broader molecular weight distribution of PBDs were obtained at higher temperature. The variation of reaction temperature had a significant influence on the microstructure of PBDs; that is, the cis-1,4 content of the resulting polymers decreased sharply and the amount of the trans-1,4 isomer increased gradually along with the elevation of reaction temperature (Fig. 1). As a result, the PBDs obtained at 90 °C contained 78.8% cis-1,4 isomer and 15.6% trans-1,4 isomer, which were largely different from the PBDs obtained at 25°C with 95.8% cis-1,4 content. Besides, the 1,2-vinyl isomer content slightly increased from 1.7% to 6.1% from 0 to 90 °C.

In order to explore the influence of the R group on the phosphine ligand, all the  $CoCl_2(PRPh_2)_2$  (1–6)–EASC catalytic systems were investigated in the solution polymerization of butadiene in toluene under the Al/Co molar ratio of 40 at 25 °C. The negligible amount of polymer obtained by  $CoCl_2$ –EASC



Fig. 1 Microstructure of PBDs produced by the 1-EASC catalytic system at different temperatures (entries 5 and 7-10 in Table 1).

under the same conditions indicated the importance of the phosphine ligand to the active centers (entry 22 in Table 1). Except for the 6 (R = H)-EASC catalytic system (conv.% = 92%, entry 15 in Table 1), all the other complexes (1-5)-EASC systems gave the complete conversions of butadiene in 60 min. In order to compare the difference between the R groups clearly, the reaction time was shortened to 10 min (entries 16-21 in Table 1) and it was observed that the R group on the phosphine ligand had an obvious influence on the catalytic activity. When the substituent R was an alkyl group, the less bulky R group led to lower conversion of butadiene (in the order of  $^{n}$ Pr > Et > Me > H) and a relatively lower molecular weight. For the cyclic R group, the 2-EASC system with the saturated cyclohexyl group showed higher catalytic activity than the 1-EASC system with the conjugated phenyl group due to the different electron-donating nature of the R groups. The cis-1,4 contents in the polymers obtained by all the complexes were in the range 94.9-97.2%. The molecular weight of PBDs produced in 10 min ranged from 89 to 153 kg mol<sup>-1</sup> with narrow molecular weight distribution (1.49-1.61). When the polymerization time was lengthened to 60 min, PBDs with lower molecular weight  $(52.5-113 \text{ kg mol}^{-1})$ and broader molecular weight distribution (2.39-2.74) were produced for each complex. It was proposed that PPh<sub>3</sub> could be a chain transfer agent when it was combined in the cobaltbased catalytic systems.<sup>27,31</sup> Speculatively, the PRPh<sub>2</sub> ligand might be an important factor to induce the chain transfer reaction and the decrease in molecular weight.

### Polymerization of butadiene in isooctane

In a typical solution polymerization of 1,3-butadiene, cyclohexane, hexane or toluene is usually used as the solvent. The selection of a non-aqueous immiscible solvent as the dispersion medium for polybutadiene is very important to perform heterogeneous polymerization of butadiene. The solubility parameter is considered to be the important basis to judge the solubility of the solute in a solvent.<sup>50</sup> When the difference of solubility parameters between the polymer and the solvent is larger than 1.5 (cal cm<sup>-3</sup>)<sup>1/2</sup>, the heterogeneous polymerization system could be generated. Isooctane ( $\delta$  = 6.85 (cal cm<sup>-3</sup>)<sup>1/2</sup>) was chosen as the dispersion medium for the heterogeneous polymerization of butadiene herein and the resultant polybutadienes ( $\delta$  = 8.60 (cal cm<sup>-3</sup>)<sup>1/2</sup>) are expected to become a powdery suspension in the medium under stirring.<sup>50–53</sup>

All the cobalt complexes (1-6)-EASC catalytic systems were used in the polymerization of butadiene with isooctane as the dispersion medium (Table 2). It was observed that the current catalytic systems were immiscible and suspended in isooctane before the butadiene solution was added. First, the different monomer concentration was used with the 1-EASC system under the Al/Co molar ratio of 80 at 25 °C (entries 1-3 in Table 3). Along with the increase in the Bd/Co molar ratio from 2000 to 4000, the conversion of butadiene declined from 95.0% to 86.9%, which was relatively lower than the

Table 2	Polymerization of	of 1,3-butadiene with	CoCl <sub>2</sub> (PRPh <sub>2</sub> ) <sub>2</sub>	(1-6)-EASC in isooctane <sup>a</sup>
---------	-------------------	-----------------------	---	--------------------------------------

Entry		Bd/Co	Al/Co	Conv. (%)	$M_{ m n}^{\ \ b} \ (10^4 \ { m g mol}^{-1})$		Microstructure <sup>c</sup> (mol%)		
	Cat.					$M_{\rm w}/M_{\rm n}^{\ b}$	<i>cis</i> -1,4-	trans-1,4-	1,2-
1	1	2000	80	95.0	0.98	3.22	87.3	7.2	5.5
2	1	3000	80	91.5	1.16	3.73	86.9	6.6	6.5
3	1	4000	80	86.9	1.37	3.92	87.3	5.6	7.1
4	1	2000	40	92.6	0.85	3.29	87.0	7.1	5.9
5	2	2000	40	100	0.93	4.56	85.8	7.4	6.8
6	3	2000	40	100	0.73	3.31	86.0	7.3	6.7
7	4	2000	40	90.9	0.72	3.15	86.2	7.4	6.4
8	5	2000	40	83.9	0.70	3.24	85.8	5.9	8.3
9	6	2000	40	49.0	0.88	2.71	81.3	5.1	13.6

<sup>*a*</sup> Polymerization conditions: cat.: 5  $\mu$ mol; cocat.: EASC; dispersion medium: isooctane, total volume: 15 mL; reaction temperature: 25 °C; reaction time: 60 min. <sup>*b*</sup> Determined by GPC against polystyrene standards and reported uncorrected. <sup>*c*</sup> Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

corresponding conversion in toluene. A consistent regularity was achieved when compared to the results in toluene under similar reaction conditions (in the orders of Cy > Ph and <sup>*n*</sup>Pr > Et > Me > H). The CoCl<sub>2</sub>(PCyPh<sub>2</sub>)<sub>2</sub> (2)- and CoCl<sub>2</sub>(P<sup>*n*</sup>PrPh<sub>2</sub>)<sub>2</sub> (3)-EASC systems also vielded 100% conversions of butadiene although the PBDs obtained had lower molecular weights and cis-1,4 contents (entries 5 and 6 in Table 2). Different from solution polymerization in toluene, a small amount of insoluble gels formed during the polymerization in isooctane, which probably can be attributed to the concentrated active species adhering onto the reactor walls because of their poor solubility in isooctane. In comparison with solution polymerization in toluene, it is clearly noted that the molecular weight of PBDs (ca.  $10^4$  g mol<sup>-1</sup>) decreased in isooctane. This behavior could be attributed to the fact of the chain transfer reaction is more favorable than propagation in isooctane, which is supported by the broader molecular weight distribution (2.71-4.56). Moreover, the microstructure of PBDs has large differences: the cis-1,4 content decreased to 81.3-87.3% and the amounts of both trans-1,4 and 1,2 isomers increased to some extent. In isooctane, the newly inserted monomer molecule is probably more favourable to tend to coordinate with only one double bond (1,2-insertion), decreasing the cis-1,4 content,

because isooctane has a lower solubility parameter than toluene ( $\delta$  = 8.90 (cal cm<sup>-3</sup>)<sup>1/2</sup>). A similar regularity can be found in a neodymium catalyst system in cyclohexane–hexane.<sup>54</sup>

#### Polymerization of butadiene in mixed solvents

In order to avoid the formation of gels, the ageing of catalysts proceeded in the mixture of toluene and isooctane to generate the homogenous solutions (Table 3). An important point should be emphasized that the volume ratio of toluene and isooctane in the ageing stage of catalysts must be equal to or larger than 1.0 to ensure the homogenization of catalytic systems. When the volume ratio of toluene and isooctane was controlled strictly at 1.0 in the ageing stage and the Bd/Co molar ratio was increased from 2000 to 4000, the conversion of butadiene slightly declined from 100% to 96.8% and the molecular weight distribution of the products increased gradually from 2.77 to 3.75 (entries 1-3 in Table 3). Keeping the monomer concentration constant (Bd/Co = 4000), the increase in toluene volume from 2.5 to 5 mL resulted in the higher molecular weight of products, but didn't greatly change the catalytic activity and the microstructure of PBDs (entries 3 and 4 in Table 3). Under the same reaction

Table 3	Polyme	rization of 1	.,3-butadie	ne with CoCl <sub>2</sub> (PRPh <sub>2</sub>	2)2 ( <b>1–6</b> )–EASC ir	n mixed solvents"				
								Microstructure <sup>d</sup> (mol%)		
Entry	Cat.	Bd/Co	Al/Co	$T-I-B-I^b$ (mL)	Conv. (%)	$M_{\rm n}^{\ c} \ \left(10^4 \ {\rm g \ mol}^{-1}\right)$	$M_{\rm w}/M_{\rm n}^{\ c}$	<i>cis</i> -1,4-	trans-1,4-	1,2-
1	1	2000	80	5/5/5	100	3.40	2.77	92.4	4.1	3.5
2	1	3000	80	4/4/7	98.6	4.98	3.50	94.2	3.0	2.8
3	1	4000	80	2.5/2.5/10	96.8	4.05	3.75	92.1	3.6	4.3
4	1	4000	80	5/0/10	97.9	5.32	3.79	92.3	3.5	4.2
5	1	2000	40	5/5/5	100	3.12	2.70	91.8	4.4	3.8
6	2	2000	40	5/5/5	100	4.08	2.92	92.7	3.9	3.4
7	3	2000	40	5/5/5	100	3.55	2.67	92.4	4.1	3.5
8	4	2000	40	5/5/5	100	3.20	2.76	92.3	3.9	3.8
9	5	2000	40	5/5/5	96.5	4.58	2.87	94.0	3.4	2.6
10	6	2000	40	5/5/5	56.1	1.07	2.23	84.3	2.9	12.8

<sup>*a*</sup> Polymerization conditions: cat.: 5  $\mu$ mol; cocat.: EASC; solvents: mixture of toluene and isooctane, total volume: 15 mL; reaction temperature: 25 °C; reaction time: 60 min. <sup>*b*</sup> T–I–B–I = toluene–isooctane–butadiene solution in isooctane ([Bd] = 2.12 mol L<sup>-1</sup>). <sup>*c*</sup> Determined by GPC against polystyrene standards and reported uncorrected. <sup>*d*</sup> Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

conditions (entries 5–10 in Table 3), complexes 1–4–EASC systems obtained the complete conversions of butadiene in 60 min and the 6–EASC system bearing the less bulky H group on the phosphine ligand gained the lower catalytic activity (conv.% = 56.1%). For all the cases of the mixed solvents, the polymerization systems became muddy with a small amount of powders and no gel was formed. The molecular weights and *cis*-1,4 content of the resultant polymers fell in between those in toluene and isooctane.

# Comparison of butadiene polymerization in toluene, isooctane and mixed solvents

Comparing the results obtained by the 1-EASC catalytic system in different solvents under similar conditions, wherein the higher concentrations of monomer and cocatalyst (Bd/Co = 4000 and Al/Co = 80) were used, the conversion of butadiene, molecular weight and cis-1,4 content of the resulting polymers declined gradually as the volume fraction of isooctane increased in the solvents (entries 3 in Table 1, 3 and 4 in Table 3, and 3 in Table 2). When the butadiene concentration and the amount of cocatalyst were reduced by half (Bd/Co = 2000 and Al/Co = 40) simultaneously, the conversion of butadiene also reached 100% in the mixed solvents and slightly decreased to 92.6% in isooctane, although both the molecular weight and cis-1,4 content of PBDs decreased gradually (entries 5 in Table 1, 5 in Table 3 and 4 in Table 2). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of PBDs obtained by the 1-EASC catalytic system in different solvents are shown in Fig. 2 and 3, respectively.

For complexes 1–4 having higher catalytic activity, the composition of solvents didn't largely affect the conversion of butadiene; however, as for complexes 5 and 6 with less bulky R groups (R = Me, H), the great influence of the isooctane fraction on the conversion of butadiene was observed (Fig. 4). The highest catalytic activity was obtained in solution polymerization; on the contrary, the heterogeneous

(a) ppm 80 7.0 60 5.0 4.0 3.0 2.0 1.0 0.0 Fig. 2 The <sup>1</sup>H NMR spectra of PBDs obtained by the 1-EASC catalytic system in toluene (a, entry 3 in Table 1), mixed solvents (b, entry 4 in

Fig. 3 The  $^{13}$ C NMR spectra of PBDs obtained by the 1–EASC catalytic system in toluene (a, entry 3 in Table 1), mixed solvents (b, entry 4 in Table 3) and isooctane (c, entry 3 in Table 2).



Fig. 4 The conversion of butadiene obtained by the  $CoCl_2(PRPh_2)_2$ (1-6)-EASC systems in different solvents. Polymerization conditions: 5 µmol of Co, Bd/Co = 2000, Al/Co = 40, T = 25 °C, t = 60 min,  $V_{total}$  = 15 mL.

polymerization in isooctane gave the lowest catalytic activity under similar conditions.

Comparing the properties of PBDs produced by complexes 1–6–EASC systems in different solvents, it was found that the *cis*-1,4 content and molecular weight of PBDs decreased gradually when isooctane was introduced into the polymerization systems (Fig. 5). The PBDs with higher molecular weight  $(5.25-11.3 \times 10^4 \text{ g mol}^{-1})$  were obtained in the homogeneous solution polymerization in toluene; while the heterogeneous polymerization in isooctane produced the PBDs with the lower molecular weight  $(0.70-0.93 \times 10^4 \text{ g mol}^{-1})$ . The molecular weight  $(1.07-4.58 \times 10^4 \text{ g mol}^{-1})$  of polymers obtained in the mixed solvents fell in between those above. The addition of isooctane into the reaction systems resulted in the decrease in *cis*-1,4 content and the increase in both *trans*-1,4 and 1,2-vinyl isomers for each complex. The PBDs

Paper

Table 3) and isooctane (c, entry 3 in Table 2).

(c)

Paper



**Fig. 5** The *cis*-1,4 content and molecular weight of PBDs produced by the CoCl<sub>2</sub>(PRPh<sub>2</sub>)<sub>2</sub> (**1-6**)-EASC systems in different solvents. Polymerization conditions: 5  $\mu$ mol of Co, Bd/Co = 2000, Al/Co = 40, T = 25 °C, t = 60 min,  $V_{\text{total}} = 15$  mL.

obtained by the 6 (R = H)-EASC system contained a larger amount of 1,2-isomers than those by other complexes.

## Conclusions

In summary, a series of phosphine-containing cobalt complexes,  $CoCl_2(PRPh_2)_2$  (R = Ph, Cy, <sup>n</sup>Pr, Et, Me, H), was proven to be highly active and stereospecific in solution polymerization of 1,3-butadiene in toluene on treatment with ethylaluminum sesquichloride (EASC). The small amount of cocatalyst (Al/Co = 40) could induce the complete conversion of butadiene and the production of PBDs with high cis-1,4 content. The bulkier R groups on the phosphine ligands led to higher catalytic activities. The dispersion medium was an important factor influencing the catalytic activity and the properties of the resulting polymers. The heterogeneous polymerization in isooctane yielded relatively lower catalytic activity, cis-1,4 content and molecular weight of PBDs under similar reaction conditions. The mixture of toluene and isooctane as a dispersion medium could avoid the formation of insoluble gels and the molecular weight and cis-1,4 content of PBDs fell in between those in toluene and isooctane.

## Experimental

### Methods and materials

All manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The molecular weight and molecular weight distribution of polybutadienes were measured by GPC using a Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards. The microstructure of polybutadienes was determined from <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra recorded using a Bruker DMX-400 instrument in CDCl<sub>3</sub> with TMS as the internal standard at room temperature.

CoCl<sub>2</sub>·6H<sub>2</sub>O was obtained from Beijing Chemical Regents Co., Ltd. and dehydrated prior to use. All the phosphine compounds [triphenylphosphine (PPh<sub>3</sub>), Sinopharm Chemical Reagent Co., Ltd.; cyclohexyldiphenylphosphine (PCyPh<sub>2</sub>), Aladdin Chemistry Co., Ltd.; propyldiphenylphosphine  $(P^nPrPh_2)$ and ethyldiphenylphosphine (PEtPh<sub>2</sub>), Tokyo Chemical Industry Co., Ltd.; and methyldiphenylphosphine (PMePh<sub>2</sub>) and diphenylphosphine (HPPh<sub>2</sub>), J&K Scientific Ltd.) were used without further purification. Ethylaluminum sesquichloride (EASC, 0.4 M in hexane) was purchased from Acros Chemicals and used directly without further purification. Toluene and isooctane were refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Polymerization grade butadiene was purified by passing it through columns of KOH and molecular sieves. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

The phosphine-containing cobalt dichloride complexes,  $CoCl_2(PRPh_2)_2$  (R = Ph (1), Cy (2), <sup>*n*</sup>Pr (3), Et (4), Me (5), H (6)), were prepared from the corresponding phosphine compound and  $CoCl_2$  in degassed ethanol in high yields according to the literature.<sup>18-20</sup>

#### Polymerization of 1,3-butadiene

The solution polymerizations of butadiene in toluene were carried out in a sealed glass reactor (100 mL) with a rubber septum and a connection to a vacuum system. The reactor was firstly charged with the desired amounts of precatalyst and cocatalyst solutions. The mixture was stirred for 2 min at various temperatures, followed by the addition of butadiene solution in toluene to start the polymerization. After the polymerization, the resulting solution was poured into a large amount of acidified ethanol (5% v/v solution of HCl) containing 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. The precipitated polymers were filtered, washed with ethanol and dried under vacuum at 50 °C overnight.

The polymerizations of butadiene in isooctane were carried out in the same way except that toluene was replaced by isooctane.

The polymerizations of butadiene in the mixed solvents were conducted in the same way except for the ageing stage of catalysts. The reactor was firstly charged with the desired amounts of precatalyst and cocatalyst in toluene and stirred for 2 min, followed by the addition of the desired amount of isooctane to form a homogenous active solution. Finally the butadiene solution in isooctane was injected into the reactor using a syringe to start the polymerization.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant no. 21006085) and the National High Technology Research and Development Program of China (grant no. 2012AA040305).

## Notes and references

- 1 A. Proto and C. Capacchione, in *Stereoselective Polymerization with Single-Site Catalysts*, ed. L. S. Baugh and J. A. M. Canich, CRC Press, Boca Raton, FL, 2008, ch. 17, pp. 447–473.
- 2 S. K. Thiele and D. R. Wilson, *J. Macromol. Sci., Polym. Rev.*, 2003, 43, 581.
- 3 L. Porri and A. Giarrusso, Compr. Polym. Sci., 1989, 4(Part II), 53.
- 4 G. J. Van Amerongen, Adv. Chem. Phys., 1966, 52, 136.
- 5 L. Porri, A. Giarrusso and G. Ricci, *Prog. Polym. Sci.*, 1991, 16, 405.
- 6 W. Cooper, Ind. Eng. Chem. Prod. Res. Dev., 1970, 9, 457.
- 7 J. Furukawa, Pure Appl. Chem., 1975, 42, 495.
- 8 J. Furukawa, Acc. Chem. Res., 1980, 13, 1.
- 9 A. Oehme, U. Gebauer, K. Gehrke and M. D. Lechner, Angew. Makromol. Chem., 1996, 235, 121.
- 10 K. Endo and N. Hatakeyama, J. Polym. Sci., Part A: Polym. Chem., 2001, 39, 2793.
- 11 D. C. D. Nath, T. Shiono and T. Ikeda, *Macromol. Chem. Phys.*, 2002, 203, 756.
- 12 D. C. D. Nath, Appl. Catal., A, 2003, 238, 193.
- 13 D. C. D. Nath, T. Shiono and T. Ikeda, *Macromol. Chem. Phys.*, 2003, **204**, 2017.
- 14 G. Kwag, C. Bae and S. Kim, J. Appl. Polym. Sci., 2009, 113, 2186.
- 15 Z. Cai, M. Shinzawa, Y. Nakayama and T. Shiono, *Macromolecules*, 2009, 42, 7642.
- 16 G. Ricci, G. Leone, A. Boglia, F. Bertini and M. Canetti, Macromol. Chem. Phys., 2009, 210, 279.
- 17 M. Takeuchi, T. Shiono and K. Soga, *Macromol. Rapid* Commun., 1995, 16, 373.
- 18 G. Ricci, A. Forni, A. Boglia and T. Motta, J. Mol. Catal. A: Chem., 2005, 226, 235.
- 19 G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti and F. Bertini, *Macromolecules*, 2005, **38**, 1064.
- 20 G. Ricci, A. Forni, A. Boglia, A. Sommazzi and F. Masi, *J. Organomet. Chem.*, 2005, 690, 1845.
- 21 G. Ricci, A. Boglia, T. Motta, F. Bertini, A. C. Boccia, L. Zetta, E. Alberti, A. Famulari, P. Arosio and S. V. Meille, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, 45, 5339.
- 22 G. Leone, A. Boglia, F. Bertini, M. Canetti and G. Ricci, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 4473.
- 23 Y. Jang, P. Kim, Y. Jeong and H. Lee, *Macromolecules*, 2002, 35, 1477.
- 24 Y. Jang, P. Kim, Y. Jeong and H. Lee, *J. Mol. Catal. A: Chem.*, 2003, 206, 29.
- 25 D. C. D. Nath, T. Shiono and T. Ikeda, J. Polym. Sci., Part A: Polym. Chem., 2002, 40, 3086.
- 26 R. Cariou, J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov and M. R. J. Elsegood, *Macromolecules*, 2009, 42, 1443.
- 27 R. Cariou, J. J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov, G. J. P. Britovsek and A. J. P. White, *Dalton Trans.*, 2010, **39**, 9039.
- 28 D. Gong, W. Jia, T. Chen and K.-W. Huang, Appl. Catal., A, 2013, 464–465, 35.

- 29 I. Kim, V. Appukuttan, L. Zhang and C. Ha, *Polymer*, 2009, 50, 1150.
- 30 I. Kim, V. Appukuttan, L. Zhang, J. Y. Ha, D. Chandran, B. K. Bahuleyan and C. Ha, *J. Mol. Catal. A: Chem.*, 2010, 325, 84.
- 31 S. Jie, P. Ai and B.-G. Li, Dalton Trans., 2011, 40, 10975.
- 32 L. Chen, P. Ai, J. Gu, S. Jie and B.-G. Li, J. Organomet. Chem., 2012, 716, 55.
- 33 H. G. Yuan, G. Kalfas and W. H. Ray, J. Macromol. Sci., Polym. Rev., 1991, 31, 215.
- 34 C. Kotoulas and C. Kiparissides, *Polym. React. Eng.*, 2007, 209–232.
- 35 G. Allegra, F. Lo Giudice, G. Natta, U. Giannini, G. Fagherazzi and P. Pino, *Chem. Commun.*, 1967, 1263–1265.
- 36 P. Crewdson, D. L. Bryce, F. Rominger and P. Hofmann, Angew. Chem., Int. Ed., 2008, 47, 3454.
- 37 V. Monteil, A. Bastero and S. Mecking, *Macromolecules*, 2005, 38, 5393.
- 38 H. Ono and T. Kato, J. Polym. Sci., Part A: Polym. Chem., 2000, 38, 1083.
- 39 G. L. Burroway, G. F. Magoun and R. N. Gujarathi, Goodyear, U.S. patent 5021381, 1991.
- 40 J. N. Henderson, K. W. Donbar, J. J. Barbour and A. J. Bell, Goodyear, U.S. patent 4429085, 1984.
- 41 O. V. Smetannikov, M. S. Chinova, E. A. Mushina, V. I. Kleiner, G. N. Bondarenko and B. F. Shklyaruk, *Polym. Sci., Ser. B*, 2012, 54, 215.
- 42 B. Korthals, A. Berkefeld, M. Ahlmann and S. Mecking, Macromolecules, 2008, 41, 8332.
- 43 G. Padavattan, C. Jäkel, T. Steinke, V. Reimer, M. B. Díaz-Valenzuela, P. Crewdson and F. Rominger, *J. Organomet. Chem.*, 2010, 695, 673.
- 44 T. Knauf, G. Sylvester, C. Schmid and A. Osman, Bayer, U.S. patent 6350833, 2002.
- 45 L. Friebe, O. Nuyken and W. Obrecht, *Adv. Polym. Sci.*, 2006, 204, 1.
- 46 G. Ricci, A. Sommazzi, F. Masi, M. Ricci, A. Boglia and G. Leone, *Coord. Chem. Rev.*, 2010, 254, 661 (and references therein).
- 47 D. Chandran, C. H. Kwak, C. S. Ha and I. Kim, *Catal. Today*, 2008, 131, 505.
- 48 P. Ai, L. Chen, Y. Guo, S. Jie and B.-G. Li, J. Organomet. Chem., 2012, 705, 51.
- 49 D. Gong, X. Jia, B. Wang, X. Zhang and L. Jiang, *J. Organomet. Chem.*, 2012, 702, 10.
- 50 I. M. Smallwood, in *Handbook of organic solvent properties*, Arnold, London, 1996.
- 51 A. F. M. Barton, in *Handbook of solubility parameters and other cohesion parameters*, CRC Press, 2nd edn, 1991.
- 52 V. D. W. Krevelen, in Properties of polymers, Amsterdam, 1990.
- 53 J. Brandrup, E. H. Immergut and E. A. Grulke, in *Polymer handbook*, Wiley, New York, 4th edn, 1999.
- 54 I. L. Mello, F. M. B. Coutinho, D. S. S. Nunes, B. G. Soares, M. A. S. Costa and L. C. Santa Maria, *Eur. Polym. J.*, 2004, 40, 635.