

IN SITU MONITORING OF COORDINATION COPOLYMERIZATION OF BUTADIENE AND ISOPRENE VIA ATR-FTIR SPECTROSCOPY*

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Abstract FTIR spectroscopy in combination with a diamond tipped attenuated total reflectance (ATR) immersion probe was utilized to study *in situ* the copolymerization of butadiene (Bd) and isoprene (Ip) with neodymium-based catalyst in hexane. The relationship between the signal intensity of monomer and its concentration was investigated. The kinetic study of copolymerization of Bd and Ip was further conducted, and the monomer reactivity ratios were determined *via in situ* ATR FTIR. The signal band at 1010 cm^{-1} was assigned to wagging vibration of Bd and its intensity was proportional to Bd concentration ($[Bd]$) in the range of $0.46\text{--}3.88\text{ mol}\cdot\text{L}^{-1}$. The signal bands at 890 and 989 cm^{-1} were assigned to wagging vibration of Ip and the signal intensity was also proportional to Ip concentration ($[Ip]$) in the range of $0.08\text{--}4.73\text{ mol}\cdot\text{L}^{-1}$ at 890 cm^{-1} and $0.08\text{--}7.49\text{ mol}\cdot\text{L}^{-1}$ at 989 cm^{-1} , respectively. Thus the signal band at 1010 cm^{-1} was chosen to monitor Bd concentration and bands at 989 and 890 cm^{-1} to monitor Ip concentration during the copolymerization, respectively. It was demonstrated that the conversions of Bd and Ip calculated from FTIR data agreed very well with those obtained gravimetrically. The polymerization rates were first order with respect to both $[Bd]$ and $[Ip]$, respectively at different polymerization temperatures. The apparent propagation activation energy for Bd and Ip could be determined to be $54.4\text{ kJ}\cdot\text{mol}^{-1}$ and $57.7\text{ kJ}\cdot\text{mol}^{-1}$, respectively. The monomer reactivity ratios were calculated to be 1.08 for Bd (r_{Bd}) and 0.48 for IP (r_{Ip}) based on FTIR data. The Bd-IP copolymer products with random sequence could be obtained with only one glass transition temperature.

Keywords: *In situ* ATR-FTIR; Butadiene; Isoprene; Copolymerization.

INTRODUCTION

Catalysts based on neodymium (Nd) and praseodymium (Pr) are well known as excellent catalysts for the stereospecific polymerization of conjugated diene, such as butadiene (Bd) and isoprene (Ip)^[1]. The kinetics of the homopolymerization of Bd or Ip using both binary and ternary catalyst systems, such as $\text{Pr}(\text{C}_6\text{H}_5\text{COCHCOCH}_3)_3/\text{Al}(\text{C}_2\text{H}_5)_3$, heterogeneous catalyst system isopropoxyneodymium dichloride/ $\text{Al}(\text{C}_2\text{H}_5)_3$ and neodymium naphthenate ($\text{Nd}(\text{naph})_3$)/ $\text{Al}(i\text{-C}_4\text{H}_9)_3/\text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$, have been investigated^[1–6]. It has been demonstrated that the homopolymerization rate was first order with respect to monomer concentration by conventional gravimetry method or by special dilatometer method^[1–4]. However, there are few investigations on the kinetics of copolymerization of Bd with Ip. The $\text{Nd}(\text{naph})_3/\text{Al}(i\text{-C}_4\text{H}_9)_3/\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ ^[1] and $\text{NdCl}_3/\text{C}_2\text{H}_5\text{OH}/\text{Al}(\text{C}_2\text{H}_5)_3$ ^[7] catalytic systems were utilized for copolymerization of Bd and Ip, and the kinetics

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of copolymerization was investigated by conventional gravimetry. The polymerization rate increased with increasing polymerization temperature and was second order with respect to the total monomer concentration ($[Bd + Ip]$), since it was difficult to real-time determine each monomer conversion during copolymerization.

The monomer reactivity ratios in the copolymerization of Bd and Ip with rare earth catalysts had been examined by Finman-Rose method at low monomer conversions (below 15%)^[7] or at high monomer conversions^[1, 8]. The values of reactivity ratios of Bd (r_{Bd}) and Ip (r_{Ip}) were dependent on the catalyst systems, and there were three cases as following^[1, 7, 8]. First, both r_{Bd} and r_{Ip} were less than 1.0 ($r_{Bd} = 0.80$, $r_{Ip} = 0.14$) for the catalyst system based on thulium (T_m)^[7]. Secondly, r_{Bd} was larger than 1.0 ($r_{Bd} = 1.10$ – 1.76) while r_{Ip} was less than 1.0 ($r_{Ip} = 0.72$ – 0.90) for the catalyst systems based on lanthanum (La), Pr, Nd, gadolinium (Gd), or yttrium (Y)^[7]. Thirdly, both the r_{Bd} and r_{Ip} were larger than 1.0, in which $r_{Bd} = 1.17$ – 2.0 , $r_{Ip} = 1.03$ – 1.04 for the cerium (Ce) or samarium (Sm) chloride, ethyl alcohol and aluminum alkyl catalyst systems^[7] or $r_{Bd} = 1.3$ – 2.0 , $r_{Ip} = 1.5$ – 2.6 for $Ln(naph)_3/Al(i-C_4H_9)_3$ or $Al(i-C_4H_9)_2H/Al(i-C_4H_9)_2Cl$ ($Ln = Nd, Pr, La$ and Ce) catalyst systems^[1, 8]. The composition of resultant copolymers was determined by pyrolytic chromatography^[7] or FTIR^[1, 8].

In situ monitoring is an efficient technique to determine instantaneous monomer concentration for homo- and co-polymerization and then obtain kinetic information and monomer reactivity ratios conveniently, which is difficult to be conducted by conventional off-line techniques^[9–12]. In the research area of copolymerization, a few studies have been reported in which the *in situ* monitoring techniques were used for determining monomer concentration. The on-line Raman spectroscopy was used to measure the partial conversion during the free radical copolymerization of styrene and butyl acrylate^[13]. The on-line ^1H -NMR spectroscopy was applied to determine the kinetic parameters and monomer reactivity ratios of radical copolymerization of styrene and itaconic acid or ethyl acrylate^[14, 15]. The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) has also been used to investigate the free-radical, anionic or cationic copolymerization^[16–19]. The *in situ* near-infrared (NIR) spectroscopy was utilized to monitor monomer conversion during the solution anionic copolymerization of styrene with isoprene, and a first-order kinetic plot was constructed^[16]. The monomer reactivity ratios in free-radical copolymerization of acrylonitrile and methyl acrylate were determined from low conversion data using a nonlinear method *via* the real-time FTIR monitoring^[17, 18]. An approach utilizing real-time FTIR data to determine the reactivity ratios in the cationic copolymerization of isobutylene and isoprene from a single experiment has been developed^[19].

In our previous work^[20–22], the neodymium-based catalysts ($Nd/Al/Cl$) had been found to exhibit both high catalytic activity and stereoselectivity for the polymerization of Bd and styrene. In this paper, the solution coordination copolymerization of Bd and Ip with $Nd/Al/Cl$ catalyst will be monitored by *in situ* ATR-FTIR spectroscopy to obtain a large number of data points of partial monomer concentration. Kinetic study on the copolymerization of Bd and Ip will be further conducted and the monomer reactivity ratios will be determined *via* real time ATR-FTIR monitoring.

EXPERIMENTAL

Materials

Butadiene (Bd), triisobutyl aluminum in hexane ($[Al(i-Bu)_3] = 0.74 \text{ mol}\cdot\text{L}^{-1}$) and 2,6-di-*tert*-butyl-4-methylphenol from Beijing Yansan Petrochemical Company were used as received. Both hexane (Hex) and isoprene (Ip) from Beijing Yansan Petrochemical Company were distilled over calcium hydride before use, respectively. The $Nd/Al/Cl$ ternary catalyst was prepared according to our previous work^[20–22]. Ethanol and hydrochloric acid were purchased from Beijing Chemical Company in China and used without further purification.

Copolymerization Procedure and *in situ* Data Collection

All polymerizations were carried out under an atmosphere of dry nitrogen. Butadiene and isoprene mixed solution in hexane was introduced into a glass reactor, and the attenuated total reflection (ATR) probe was

immersed into the polymerization solution. The catalyst was added through a syringe to start the copolymerization at a definite temperature, and the copolymerization process was monitored by the ATR probe simultaneously. The FTIR spectra were recorded by a Nicolet 6700 spectrophotometer with a diamond tipped ATR immersion probe (Axiom DMD-270X-LT) as shown in Fig. 1. FTIR data collection and processing were performed with Nicolet's OMNIC Series software. The FTIR spectrum of hexane was chosen as the background for spectrum record. Each spectrum was collected every 24 s by accumulating 24 scans with an instrument resolution of 4 cm^{-1} over the spectral range of $600\text{--}1800\text{ cm}^{-1}$. For parallel gravimetical analysis of conversion and structural characterization, about 10 mL of polymer solution was taken out from the polymerization system at different specified time and then terminated by adding ethanol and 2,6-di-*tert*-butyl-4-methylphenol. The resultant copolymer was washed by ethanol and then water until neutral and finally dried under vacuum at 45°C to constant weight.

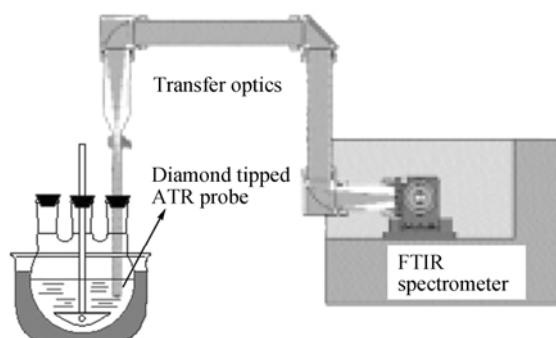


Fig. 1 Experimental set-up for the *in situ* monitoring of copolymerization

Copolymer Characterization

The differential scanning calorimetry (DSC) scans were carried out on a TA Q200 instrument equipped with a liquid subambient device. About 8 mg copolymer were weighted into an aluminum pan and heated from -150°C to 40°C under a helium atmosphere ($25\text{ mL}\cdot\text{min}^{-1}$) at a scan rate of $10\text{ K}\cdot\text{min}^{-1}$. The FTIR spectra of copolymers were recorded using films on KBr plate by a Nicolet 6700 spectrophotometer as the average of 64 acquisitions over the spectral ranges of $400\text{--}2000\text{ cm}^{-1}$ with an instrument resolution of 4 cm^{-1} . The composition of resultant copolymers was determined by FTIR according to the reference^[23].

RESULTS AND DISCUSSION

Determination of Monomer Concentration by ATR-FTIR

The FTIR spectra of the Bd solution, Ip solution and the mixture solution of Bd and Ip in hexane ($[\text{Bd}] = [\text{Ip}] = 1.5\text{ mol}\cdot\text{L}^{-1}$) collected by an ATR probe and the descriptions are given in Fig. 2. The signal bands at 1010 and 989 cm^{-1} are assigned to the wagging vibrations of $\text{C}-\text{H}^{\text{a}}$ and $\text{C}-\text{H}^{\text{b}}$ bonds in vinyl groups of Bd and Ip, respectively. The relatively strong absorption at 890 cm^{-1} is assigned to the wagging vibrations of $\text{C}-\text{H}^{\text{d}}$ and $\text{C}-\text{H}^{\text{e}}$ bonds in vinylidene groups of Ip. The signal at 904 cm^{-1} is assigned to the wagging vibrations of $\text{C}-\text{H}^{\text{b}}$ and $\text{C}-\text{H}^{\text{c}}$ bonds in vinyl groups of both Bd and Ip. It was found that the intensity of bands at 989 , 890 and 1010 cm^{-1} of mixture solutions was almost in accordance with that of Bd solutions or Ip solutions. Therefore, the signal band at 1010 cm^{-1} could be chosen for monitoring Bd conversion and that at 989 cm^{-1} or 890 cm^{-1} for monitoring Ip conversion during the copolymerization.

The FTIR spectra of Bd solution and Ip solution at different concentrations were recorded by ATR probe respectively. The relationship between signal intensity and monomer concentration is shown in Figs. 3(a) and 3(b) for Bd solution and Ip solution, respectively. It can be observed from the plots that the linearity between the signal intensity and the monomer concentration could be obtained when the monomer concentration was below the corresponding critical values. The appropriate monomer concentration range was established based

on the linear plots and the experimental data. Bd concentration ($[Bd]$) was proportional to the intensity of band at 1010 cm^{-1} in the range of $0.46\text{--}3.88\text{ mol}\cdot\text{L}^{-1}$. Ip concentration ($[Ip]$) was proportional to the intensity of band at 890 cm^{-1} in the range of $0.08\text{--}4.73\text{ mol}\cdot\text{L}^{-1}$ or at 989 cm^{-1} in the range of $0.08\text{--}7.49\text{ mol}\cdot\text{L}^{-1}$. It can be induced from the linearity that the signal bands of monomers could reflect the concentration of Bd and Ip in the corresponding monomer range respectively.

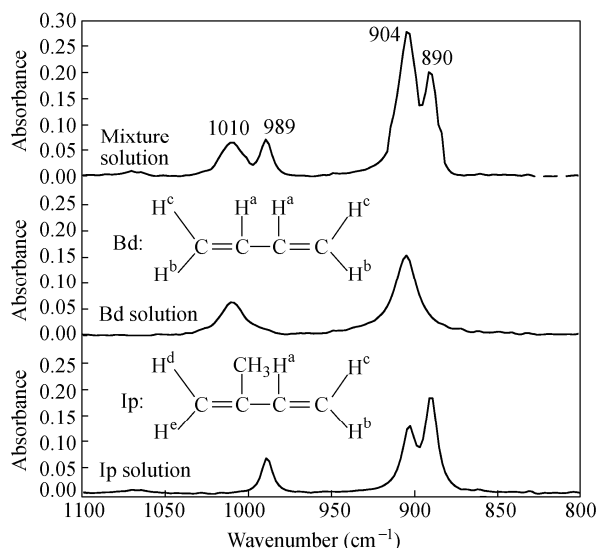


Fig. 2 ATR-FTIR spectra of Bd solution, Ip solution and mixture solution of Bd and Ip in hexane
The FTIR spectrum of hexane was taken as the background;
 $[Bd] = 1.5\text{ mol}\cdot\text{L}^{-1}$; $[Ip] = 1.5\text{ mol}\cdot\text{L}^{-1}$; 0°C

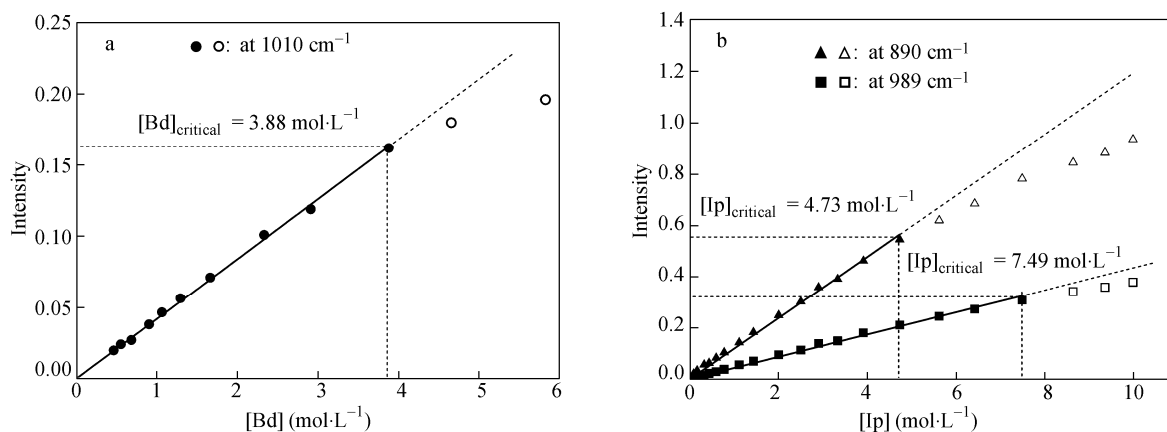


Fig. 3 The plots of signal intensity with monomer concentration (a) Bd, (b) Ip
The spectra were constructed from 32 scans.

Kinetic Study on the Copolymerization of Bd with Ip

The copolymerization of Bd and Ip was carried out in hexane at 22°C under the conditions of $[Bd]_0 = 1.44\text{ mol}\cdot\text{L}^{-1}$ and $[Ip]_0 = 0.77\text{ mol}\cdot\text{L}^{-1}$. The conversions of Bd (C_{Bd}) and Ip (C_{Ip}) at 150 min were determined to be 44% and 37%, respectively by conventional gravimetical measurements according to the Eqs. (1) and (2). Namely, $[Bd]$ decreased from $1.44\text{ mol}\cdot\text{L}^{-1}$ to $0.81\text{ mol}\cdot\text{L}^{-1}$ and $[Ip]$ from $0.77\text{ mol}\cdot\text{L}^{-1}$ to $0.49\text{ mol}\cdot\text{L}^{-1}$ during copolymerization. Thus, $[Bd]$ and $[Ip]$ during the copolymerization could be also determined by *in situ* ATR-FTIR on the basis of the linear plots and the corresponding monomer concentration shown in Fig. 3.

$$C_{\text{Bd}} = W_p \times F_{\text{Bd}} / (V \times [\text{Bd}]_0 \times 54.1) \times 100 \quad (1)$$

$$C_{\text{Ip}} = W_p \times (1 - F_{\text{Bd}}) / (V \times [\text{Ip}]_0 \times 68.1) \times 100 \quad (2)$$

Where W_p is weight of copolymer obtained, F_{Bd} is copolymer composition calculated from the corresponding FTIR spectra of the copolymers^[23].

Figure 4 illustrates the waterfall plots of monomers during the copolymerization monitored by *in situ* ATR-FTIR. It can be clearly observed that the intensity of the corresponding signals decreased gradually with polymerization time. According to Eqs. (3), (4) and (5), both the real time [Bd] and [Ip] could be determined, and a large number of data are shown in Fig. 5. It can be seen that both [Bd] and [Ip] decreased gradually with polymerization time, which indicated that both Bd and Ip were consumed simultaneously during the copolymerization and Bd conversion appeared to be slightly faster than Ip conversion.

$$[\text{Bd}]_t = A_{1010,t} / A_{1010,0} \times [\text{Bd}]_0 \quad (3)$$

$$[\text{Ip}]_t = A_{890,t} / A_{890,0} \times [\text{Ip}]_0 \quad (4)$$

$$[\text{Ip}]_t = A_{989,t} / A_{989,0} \times [\text{Ip}]_0 \quad (5)$$

Where the subscripts 0 and t denote the corresponding value obtained at the beginning and at polymerization time t , respectively; A_{1010} , A_{890} and A_{989} are the intensity of bands at 1010, 890 and 989 cm^{-1} , respectively.

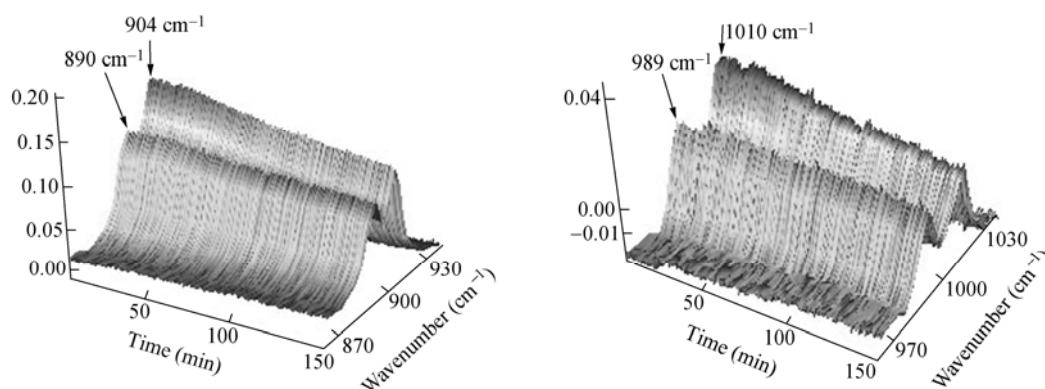


Fig. 4 *In situ* FTIR spectra of an Bd/IP copolymerization

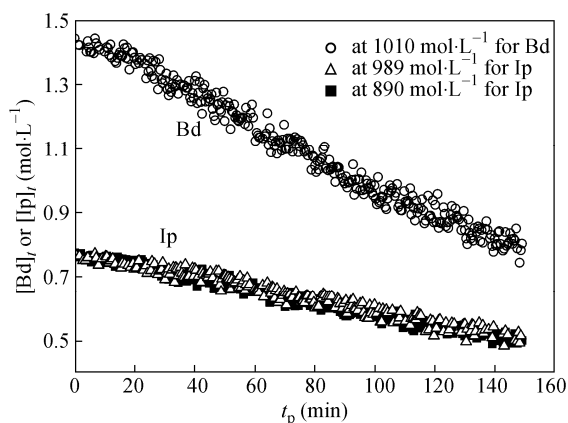


Fig. 5 The plots of Bd concentration and Ip concentration with polymerization time (t_p)

The conversions of Bd and Ip obtained from FTIR were calculated on the basis of the $[Bd]_t$ and $[Ip]_t$ shown in Fig. 5 respectively. It can be seen from Fig. 6 that the conversions of Bd and Ip calculated by conventional gravimetric measurement based on the Eqs. (1) and (2) are almost in accordance with the conversion data obtained from the *in situ* ATR-FTIR monitoring. The Ip conversion calculated on the basis of the signal intensity at 989 cm^{-1} agreed very well with that at 890 cm^{-1} , and thus the stronger signal band at 890 cm^{-1} was selected for the further calculation of Ip conversion. Therefore, kinetic information could be readily obtainable from the real-time FTIR spectra data.

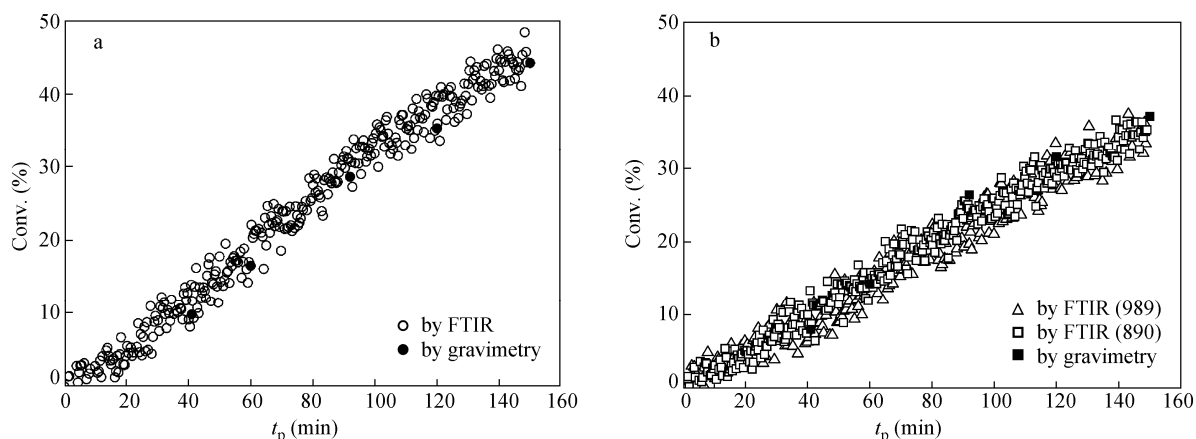


Fig. 6 The plots of conversion of (a) Bd and (b) Ip with polymerization time (t_p) on the basis of FTIR and gravimetry data

The first-order plots were constructed for Bd and Ip at different polymerization temperatures respectively. As shown in Fig. 7, The linearity plots of $\ln([M]_0/[M])$ with polymerization time demonstrate that the polymerization rate is first order with respect to monomer concentration for both Bd and Ip. The apparent rate constant of propagation for Bd ($k_{p,Bd}^A$) and Ip ($k_{p,Ip}^A$) were obtained from the slope of linear plots for each experimental set at different polymerization temperatures. It can be seen that $k_{p,Bd}^A$ is slightly larger than $k_{p,Ip}^A$ at the same temperature, and both $k_{p,Bd}^A$ and $k_{p,Ip}^A$ increase with increasing temperature from 0°C to 28°C . The Arrhenius plots of $\ln k_{p,Bd}^A$ or $\ln k_{p,Ip}^A$ versus the reciprocal of absolute temperature ($1/T$) are linear for both Bd and Ip, as shown in Fig. 8. The apparent activation energy for Bd and Ip could be determined to be 54.4 and $57.7\text{ kJ}\cdot\text{mol}^{-1}$, respectively.

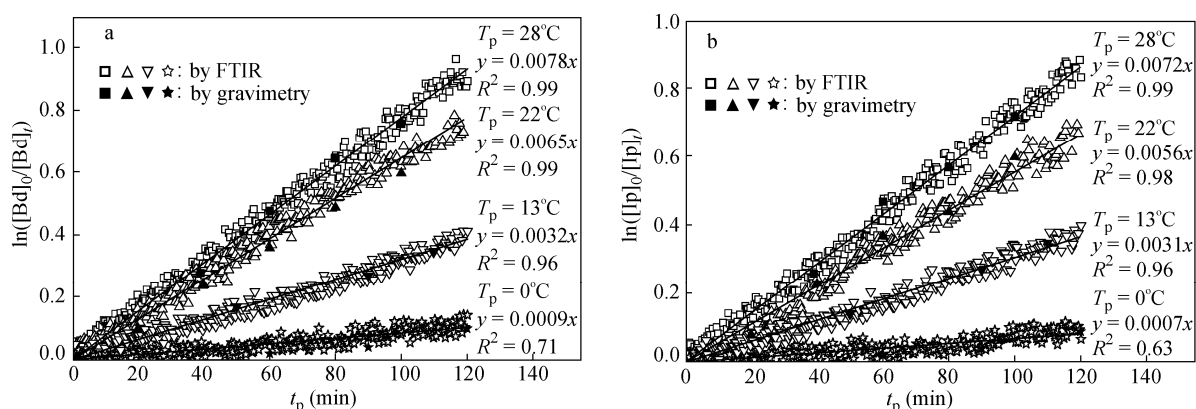


Fig. 7 First-order plots for Bd (a) and Ip (b) at various polymerization temperatures

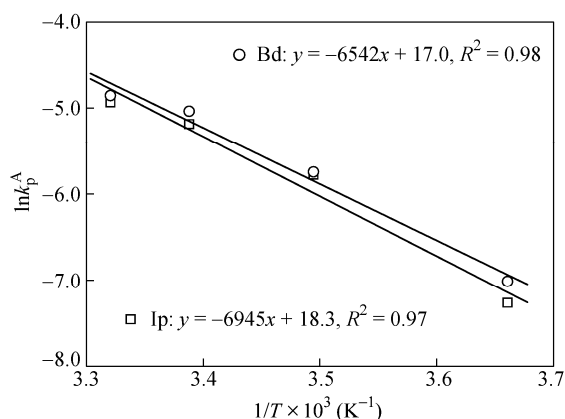


Fig. 8 The relationship between $\ln k_p^A$ and $1/T$ for Bd and Ip

Monomer Reactivity Ratios

In order to determine the monomer reactivity ratios, the copolymerization of Bd with Ip was carried out at different molar contents of Bd in feed ($f_{Bd} = 39.7\% - 83.3\%$) while keeping other reaction conditions constant. *In situ* ATR-FTIR was used to monitor the copolymerization process, and a large number of data points were obtained. When the data from *in situ* FTIR were used to calculate monomer reactivity ratios, sets of data point pairs were considered as individual low conversion experiments. Instantaneous differential monomer consumption was assumed to be equal to the instantaneous copolymer composition and was calculated based on the linear fit of $\ln([Bd]_0/[Bd]_t)$ and $\ln([Ip]_0/[Ip]_t)$. The $d[Bd]_t$ and $d[Ip]_t$ were calculated from FTIR data as shown by Eqs. (6) and (7)^[19]:

$$d[Bd]_t = [Bd]_{t+\Delta t} - [Bd]_t \quad (6)$$

$$d[Ip]_t = [Ip]_{t+\Delta t} - [Ip]_t \quad (7)$$

The time interval between two consecutive data points was 24 s in our study.

First, the Fineman-Ross equation was employed to calculate the monomer reactivity ratios^[24]:

$$F_{Bd}(1-2F_{Bd})/(F_{Bd}(1-f_{Bd})) = r_{Ip} + r_{Bd}f_{Bd}^2(F_{Bd}-1)/(F_{Bd}(1-f_{Bd})^2) \quad (8)$$

where $f_{Bd} = [Bd]_t/([Bd]_t + [Ip]_t)$; $F_{Bd} = d[Bd]_t/(d[Bd]_t + d[Ip]_t)$.

From the slope and intercept of the plot of $F_{Bd}(1-2F_{Bd})/(F_{Bd}(1-f_{Bd}))$ versus $f_{Bd}^2(F_{Bd}-1)/(F_{Bd}(1-f_{Bd})^2)$ in Fig. 9, the reactivity ratios r_{Bd} and r_{Ip} were determined to be 1.08 and 0.48, respectively.

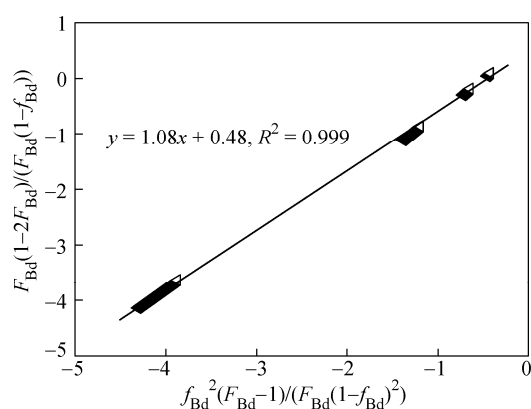


Fig. 9 Fineman-Ross plot for copolymerization of Bd and Ip

Secondly, the Kelen-Tüdös method was also employed to calculate monomer reactivity ratios^[25]. It is insensitive to indexation, and a symmetric distribution of data points may be achieved. The Kelen-Tüdös equation is given as following:

$$\eta = [r_{\text{Bd}} + r_{\text{Ip}}/\alpha] \xi - r_{\text{Ip}}/\alpha \quad (9)$$

where $\eta = G/(\alpha + F)$; $\xi = F/(\alpha + F)$; $X = [\text{Bd}]_0/[\text{Ip}]_0$; $Y = d[\text{Bd}]/d[\text{Ip}]_0$; $G = X(Y-1)/Y$; $F = X^2/Y$; $\alpha = (F_{\text{max}}F_{\text{min}})^{0.5}$

Instantaneous values of η and ξ were calculated from Eq. (9). From the slope and intercept of the η versus ξ plot in Fig. 10, the reactivity ratios r_{Bd} and r_{Ip} could be further calculated to be 1.10 and 0.51 according to the Eq. (9). The reactivity ratios r_{Bd} and r_{Ip} by the Kelen-Tüdös method are in excellent agreement with the corresponding data evaluated by the Fineman-Ross method ($r_{\text{Bd}} = 1.08$; $r_{\text{Ip}} = 0.48$). The values of reactivity ratios indicate that the homopolymerization rate of Bd is almost close to the rate of copolymerization with Ip, while Ip is more benefit to copolymerization with Bd, resulting in the formation of random copolymers of Bd with Ip.

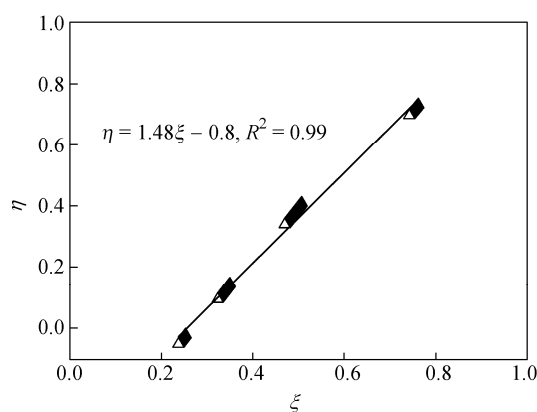


Fig. 10 Kelen-Tüdös plot for copolymerization of Bd and Ip
 $F_{\text{max}} = 4.31$, $F_{\text{min}} = 0.42$, $\alpha = 1.35$

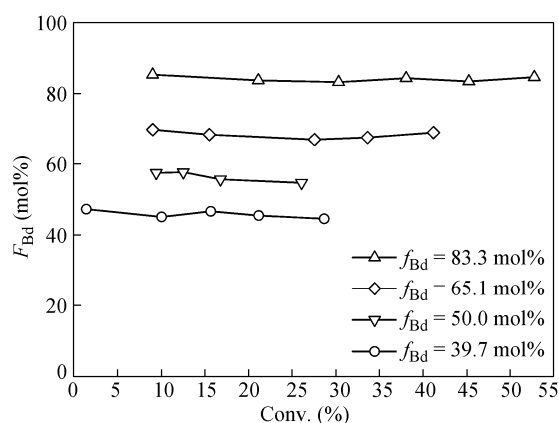


Fig. 11 The relationship between the Bd content in copolymer with total monomer conversion

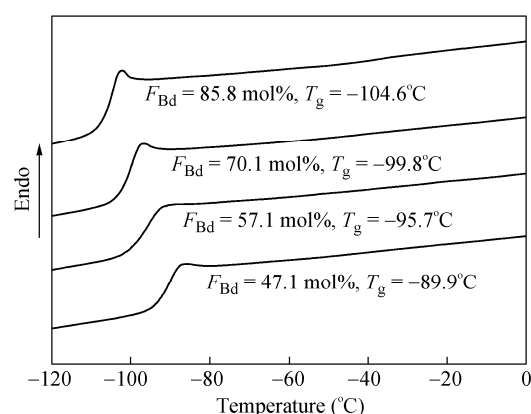


Fig. 12 DSC heating curves of the resultant copolymers with different compositions

As shown in Fig. 11, the Bd contents in copolymers (F_{Bd}) were nearly closed to those in monomer feed (f_{Bd}) at 65.1 mol% or 83.3 mol%, while they were slightly higher than those in monomer feed (f_{Bd}) at 39.7 mol% or 50.0 mol%. Copolymer composition did almost unchanged with increasing total monomer conversion (Conv.%), which indicates that the copolymer products were indeed in random sequence. Only one glass transition

temperature (T_g) for the copolymers with Bd contents from 44.5 mol% to 84.6 mol% is observed in DSC curves (shown in Fig. 12), which is another evidence of random copolymer sequence.

CONCLUSIONS

ATR-FTIR spectroscopy was successfully used to monitor the solution copolymerization process of butadiene (Bd) and isoprene (Ip) with Nd-based catalyst in hexane. The signal band at 1010 cm^{-1} for Bd was proportional to its concentration in the range of $0.46\text{--}3.88\text{ mol}\cdot\text{L}^{-1}$. Both the signal bands at 890 and 989 cm^{-1} for Ip were proportional to Ip concentration in the range of $0.08\text{--}4.73\text{ mol}\cdot\text{L}^{-1}$ and $0.08\text{--}7.49\text{ mol}\cdot\text{L}^{-1}$, respectively. These three signal bands could be selected for real time monitoring the instantaneous concentrations of Bd and Ip during their copolymerization respectively. The polymerization rates was first order with respect to both the Bd and Ip concentrations, and the apparent activation energy for Bd and Ip was determined to be 54.4 and $57.7\text{ kJ}\cdot\text{mol}^{-1}$, respectively. The reactivity ratios of Bd and Ip could be determined to be 1.08 and 0.48 , respectively. The Bd content in copolymer (F_{Bd}) was nearly closed to that in monomer feed (f_{Bd}) at high f_{Bd} of more than 65 mol%. The copolymer composition was independent of the copolymerization conversion, and only one glass transition temperature was observed in the DSC curves of resultant random copolymers.

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