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Polymerization of 1,3-butadiene with $VO(P_{204})_2$ and $VO(P_{507})_2$ activated by alkylaluminum

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Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

The oxovanadium phosphonates ($VO(P_{204})_2$ and $VO(P_{507})_2$) activated by various alkylaluminums (AlR_3, R = Et, *i*-Bu, *n*-Oct; $HAlR_2$, R = Et, *i*-Bu) were examined in butadiene (Bd) polymerization. Both $VO(P_{204})_2$ and $VO(P_{507})_2$ showed higher activity than those of classical vanadium-based catalysts (e.g. $VOCl_3$, $V(acac)_3$). Among the examined catalysts, the $VO(P_{204})_2/Al(Oct)_3$ system (I) revealed the highest catalytic activity, giving the poly(Bd) bearing M_n of 3.76×10^4 g/mol, and M_w/M_n ratio of 2.9, when the [Al]/[V] molar ratio was 4.0 at 40 °C. The polymerization rate for I is of the first order with respect to the concentration of monomer. High thermal stability of I was found, since a fairly good catalytic activity was achieved even at 70 °C (polymer yield > 33%); the M_n value and M_w/M_n ratio were independent of polymerization temperature in the range of 40–70 °C. By IR and DSC, the poly(Bd)s obtained had high 1,2-unit content (>65%) with atactic configuration. The 1,2-unit content of the polymers obtained by I was nearly unchanged, regardless of variation of reaction conditions, i.e. [Al]/[V], ageing time, and reaction temperature, indicating the high stability of stereospecificity of the active sites.

Keywords: Butadiene; Vanadium; 1,2-Poly(butadiene)

1. Introduction

Vanadium-based (V-based) catalysts have been widely studied in the field of polymerization of ethylene, propylene and 1,3-butadiene (Bd), since they are used for preparing ethylene/propylene/diene (EPDM) elastomers, *trans*-1,4 and syndiotactic-1,2 poly(Bd)s and so on [1,2]. In olefin polymerization, the quality of EPDM obtained by V-based catalysts is unique, which makes these catalytic systems irreplaceable, even though they still suffer from poor activity [3]. In the case of Bd polymerization, with the chloride-containing catalysts derived from $V(acac)_3$ or $VCl_3 \cdot 3THF$ and AlR_2Cl or $AlRCl_2$, *trans*-1,4 poly(Bd) was produced [4–7]; while with the chloride-free catalysts, such as $V(acac)_3/AlR_3$, syndiotactic 1,2-poly(Bd)s was produced [8,9]. Note that these Bd polymerization catalysts required a high molar ratio of [V]/[Bd], and low polymerization temperature (≤20 °C) was essential, thus polymer in rather low yield was obtained (≤40%). Although some promoted activity of V-based catalyst was found when activated with methylaluminoxane (MAO), the fluctuation of the microstructure with polymerization conditions and a rather high [MAO]/[V] ratio required make these systems unpractical [10–13]. As consequence, further applications of V-based catalyst for Bd polymerization were depressing.

In our previous study [14], the complex of $VO(P_{204})_2$ was found to be less sensitive to air and moisture than the above-mentioned V-based catalysts. When combined with $Et_3Al_2Cl_3$, the $VO(P_{204})_2$ system exhibited much higher catalytic activity and longer active life than that of the $VOCl_3/Et_3Al_2Cl_3$ system in the copolymerization of ethylene and propylene. These

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encouraging results prompted us to investigate the behavior of oxovanadium phosphonate in Bd polymerization for the synthesis of 1,2-poly(Bd), which is potential for practical applications as we discussed in Bd polymerization with the Fe-based system [15].

2. Experimental part

2.1. Materials

Bd was donated by Jinzhou Petrochemical Company, Petrochina and dried by passing through a column packed with KOH and 4 Å molecular sieves. Commercially available AlR_3 (R = Et, *i*-Bu, *n*-Oct) and $HAlR_2$ (R = Et, *i*-Bu) were used without purification. Oxovanadium phosphonate of $VO(P_{204})_2$ was prepared according to the procedure described in Ref. [16], and the same procedure was used to synthesize vanadium complex of $VO(P_{507})_2$. The structures of P_{204} and P_{507} are shown in Fig. 1. Toluene (Beijing Reagents Factory) was refluxed over sodium benzophenone ketyl under nitrogen until the solution turned blue and distilled before use.

2.2. Polymerization

All the manipulations were performed under a dry nitrogen atmosphere. A detailed polymerization procedure (line 3 of Table 1) is described as a typical example. At first, a solution of Bd in toluene was prepared as the method described below: Bd was condensed into a vessel with volume grading, cooled at 0 °C and added via a bridge into the flask precontaining the toluene. The Bd concentration (1.85 mol/L) was determined by weighing the vessel before charging it with toluene and before and after adding the Bd. The solution was divided via a distributor into portions (40 mL per portion) and transferred to an ampule bottle. After the reaction solution was heated to the desired temperature in a water-bath, $VO(P_{204})_2$ (1.85×10^{-1} mol/L solution in toluene, 0.40 mL), and $Al(Oct)_3$ (1.0 mol/L solution in toluene, 0.30 mL) were introduced into the reaction solution via syringes. Polymerization was carried out at 40 °C for 2 h and quenched by adding acidified ethanol containing 2,6-di-*tert*-butyl-*p*-methylphenol (1 wt%) as a stabilizer. The formed polymer was coagulated, repeatedly washed with ethanol, and finally dried under vacuum at 40 °C to constant weight.

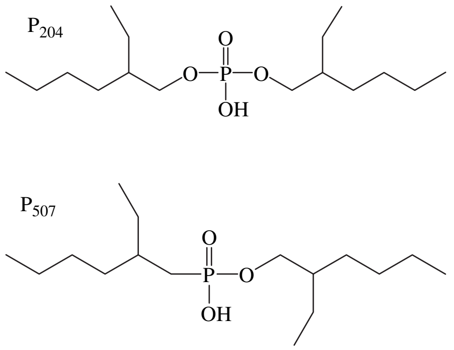

Fig. 1. The structures of P_{204} and P_{507}.

2.3. Polymer characterization

The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured at 30 °C by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF) and a Waters 2414 refractive index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. The molecular weights of poly(Bd) were determined using the polystyrene calibration. Sample solutions (1.0 mg/mL) were filtered through a 0.45 μm microfilter before injection.

The IR spectroscopy was used to determine the microstructure of Bd units and recorded on a Bio-Rad FIS 135 Spectrophotometer using a film sample. DSC was measured on a Perkin–Elmer Diamond DSC instrument at a heating rate of 10 °C/min from −50 to 200 °C using 10 mg sample.

3. Results and discussion

V-based catalysts are known for superior copolymerization properties for manufacturing EPDM, and synthesizing polydienes in versatile chain structures [1,2]. In spite of the industrial application in olefin copolymerization, V-based catalyst still suffers from low activity, low polymerization temperature required and short life time [3]. The situation becomes even worse in diene polymerization, where besides the disadvantages showed in olefin polymerization, the microstructure of polydienes varies with polymerization conditions, such as the ratios of catalyst components and polymerization temperature, which is an additional undesirable aspect.

We have synthesized oxovanadium phosphonates ($VO(P_{204})_2$ and $VO(P_{507})_2$) in our laboratory recently. The unique V–O–P bond may provide special characteristics in both olefin [14] and diene polymerization.

3.1. Polymerization behaviors with variation of cocatalyst

Table 1 shows the results of the polymerization of Bd with the catalyst systems derived from $VO(P_{204})_2$ and $VO(P_{507})_2$ with cocatalysts of AlR_3 (R = Et, *i*-Bu, Oct) and $HAlR_2$ (R = Et, *i*-Bu). The catalysts of $VO(P_{204})_2$ and $VO(P_{507})_2$ in combination with $Al(i\text{-}Bu)_3$ or $Al(Oct)_3$ were found to be more efficient in Bd polymerization as compared to the vanadium-based catalysts cited in the literatures [4–8], since the polymerizations could be readily initiated at a higher temperature under a relatively low molar ratio of [V]/[Bd] (ca. 1.0×10^{-3}). With regards to being activated by the same cocatalyst, the catalytic activity with $VO(P_{204})_2$ was found to be higher than that of $VO(P_{507})_2$. This might be due to the differences of Lewis basicity between the anionic ligands ($pk_a(P_{204}) = 1.30$ and $pk_a(P_{507}) = 2.34$ [17]). In the case of $VO(P_{204})_2$, the activity and M_n increased as the alkyl group (R) (in

Table 1
Variation of cocatalyst on Bd polymerization in the presence of $VO(P_{204})_2$ and $VO(P_{507})_2$ in toluene at 40 °C for 2 h (conditions: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L)

V-compound	Cocatalyst	[Al]/[V] (mol/mol)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
						cis-1,4	*trans*-1,4	1,2
$VO(P_{204})_2$	$AlEt_3$	4.0	28.9	1.27	5.2	21.6	8.2	70.2
	Al(*i*-Bu)$_3$	4.0	42.4	1.63	4.6	28.0	3.5	68.5
	$Al(Oct)_3$[a]	4.0	66.6	3.76	2.9	31.8	2.6	65.6
	$HAlEt_2$	4.0	5.7	1.32	3.9	30.1	4.7	65.2
	HAl(*i*-Bu)$_2$	4.0	11.4	1.44	9.0	16.3	13.6	70.1
$VO(P_{507})_2$	$AlEt_3$	3.0	18.5	2.21	4.1	25.8	2.8	71.4
	Al(*i*-Bu)$_3$	3.0	30.0	1.56	4.5	22.1	4.9	73.0
	$Al(Oct)_3$[a]	3.0	41.0	4.56	2.8	30.2	1.8	68.0
	$HAlEt_2$	3.0	1.7	–	–	–	–	–
	HAl(*i*-Bu)$_2$	3.0	3.9	–	–	–	–	–

[a] $Al(Oct)_3$ indicates trioctylaluminum.

alkylaluminum compound) became longer in the order of $Al(Oct)_3 > Al(i\text{-}Bu)_3 > AlEt_3 > HAl(i\text{-}Bu)_2 > HAlEt_2$. Meanwhile, M_w/M_n ratio showed inverse order for the case of AlR_3. As for active vanadium centers, the weaker reduction ability of alkylaluminum compound containing the longer R group [1] could keep the concentration of active sites at a relatively high level, and, due to bulky R group, suppressed chain transfer could narrow molecular weight distribution. The GPC profiles in Fig. 2 evidenced narrowest M_w/M_n with the monomodal distribution when $Al(Oct)_3$ was used as cocatalyst. The M_n of the poly(Bd)s for the $VO(P_{204})_2$ and $VO(P_{507})_2$ activated by $Al(Oct)_3$ were 3.76 and 4.56×10^4 g/mol, respectively, with the M_w/M_n ratios less than 3.0, implying single active sites yielding polymers bearing high M_n and relatively low M_w/M_n ratio, differentiating these catalysts from the reported V-based catalysts [7,12].

3.2. The effects of [Al]/[V] molar ratios

It is known that the ratio of catalyst components of the binary catalyst system has influences on both the activity and the microstructure of the resulted polymer, especially for vanadium and ferrum-based catalysts having variable valence. The effects of the [Al]/[V] molar ratio on the polymerization of Bd with the $VO(P_{204})_2$ and $VO(P_{507})_2$ are tabulated in Tables 2 and 3. The polymer yields increased rapidly with the increase of [Al]/[V] ratio up to 4.0 and 3.0 for the $VO(P_{204})_2/AlR_3$ and $VO(P_{507})_2/AlR_3$ systems, respectively, and then followed a slow decrease with further addition of AlR_3, while M_n and M_w/M_n ratio also showed variation in the increment of [Al]/[V] ratio. The variation in the concentration of V^{3+} active sites resulted from the variance of [Al]/[V] ratio, which could account for the results [18].

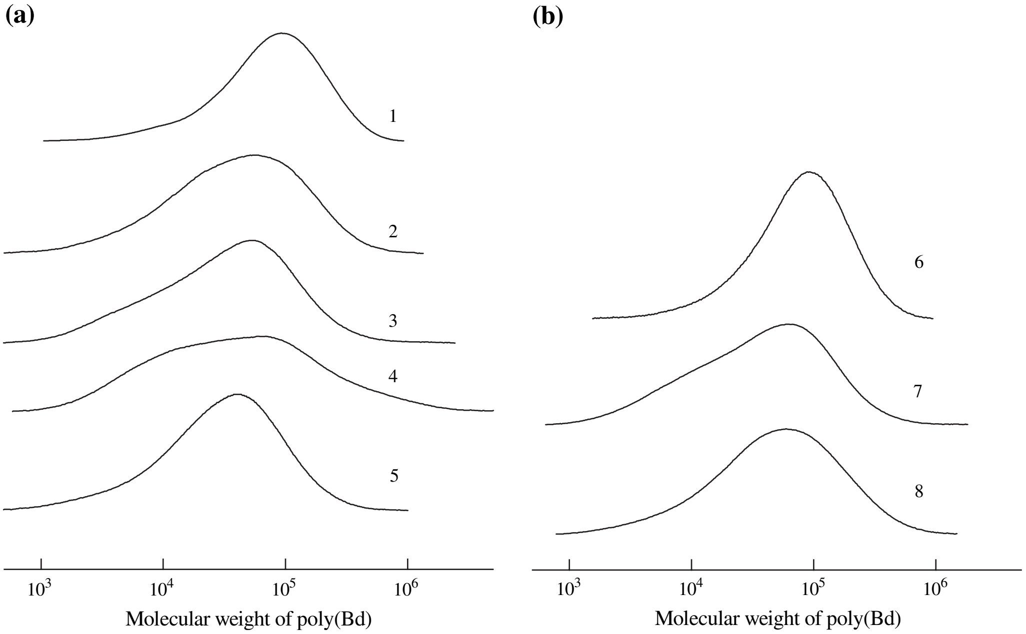

Fig. 2. GPC profiles of the poly(Bd)s with $VO(P_{204})_2$ and $VO(P_{507})_2$ activated by different alkylaluminums, (a) $VO(P_{204})_2/Al(Oct)_3$ (1), $VO(P_{204})_2$/Al(*i*-Bu)$_3$ (2), $VO(P_{204})_2/AlEt_3$ (3), $VO(P_{204})_2$/HAl(*i*-Bu)$_2$ (4), $VO(P_{204})_2/HAlEt_2$ (5); (b) $VO(P_{507})_2/Al(Oct)_3$ (6), $VO(P_{507})_2$/Al(*i*-Bu)$_3$ (7), $VO(P_{507})_2/AlEt_3$ (8). Polymerization conditions: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L, $[Al]/[VO(P_{204})_2] = 4.0$ mol/mol or $[Al]/[VO(P_{507})_2] = 3.0$ mol/mol in toluene at 40 °C for 2 h.

Table 2
Variation of [Al]/[V] molar ratio on Bd polymerization with $VO(P_{204})_2/AlR_3$ catalysts in toluene at 40 °C for 2 h (condition: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L)

Cocatalyst	[Al]/[V] (mol/mol)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
					cis-1,4	*trans*-1,4	1,2
$Al(i\text{-}Bu)_3$	3.5	28.3	n.d.[a]	n.d.[a]	26.7	3.3	70.0
	4.0	42.4	1.63	4.6	28.0	3.5	68.5
	10.0	32.1	1.57	4.8	31.3	5.3	63.4
	20.0	25.3	n.d.[a]	n.d.[a]	33.8	4.5	61.7
$Al(Oct)_3$	4.0	66.6	3.76	2.9	31.8	2.6	65.6
	5.0	66.0	2.88	2.3	33.7	2.0	64.3
	10.0	60.8	2.96	2.3	33.9	1.9	64.2
	20.0	55.2	n.d.[a]	n.d.[a]	34.2	2.0	63.8

[a] n.d. indicates not determined.

Table 3
Variation of [Al]/[V] molar ratio on Bd polymerization with $VO(P_{507})_2/AlR_3$ catalysts in toluene at 40 °C for 2 h (condition: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L)

Cocatalyst	[Al]/[V] (mol/mol)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
					cis-1,4	*trans*-1,4	1,2
$Al(i\text{-}Bu)_3$	2.5	9.0	n.d.[a]	n.d.[a]	20.7	5.0	74.3
	3.0	30.0	1.56	4.5	22.1	4.9	73.0
	5.0	23.9	1.50	4.7	23.3	4.0	72.7
	8.0	13.1	n.d.[a]	n.d.[a]	25.8	3.2	71.0
$Al(Oct)_3$	2.5	38.9	n.d.[a]	n.d.[a]	28.7	1.7	69.6
	3.0	41.0	4.56	2.8	30.2	1.8	68.0
	4.0	37.7	4.29	2.9	31.6	1.7	66.7
	8.0	36.4	3.59	3.0	33.6	0.2	66.2

[a] n.d. indicates not determined.

3.3. Ageing process on polymerization behaviors

The deactivation process of active species was estimated by ageing catalyst with different time, and the results of $VO(P_{204})_2/AlR_3$ (R = *i*-Bu, Oct) catalysts are tabulated in Table 4. When the time of catalyst ageing was prolonged from 0 to 30 min, the polymer yield decreased rapidly, while the M_n was almost unchanged, and M_w/M_n became broader. The interpretation for these phenomena could be that the active sites formed immediately when it contacted with cocatalyst; prolonging ageing time could cause active species to diversify into multiple types, and some of them were inactive or less active. Moreover, the catalyst aged in the presence of Bd monomer did not enhance the catalytic activity, either, implying that the active species was not stabilized by π-electron donation of monomer. Thus, these catalysts should be used without ageing process.

Table 4
Polymerization of Bd with aged catalysts in toluene at 40 °C for 2 h (conditions: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L, [Al]/[V] = 4.0 mol/mol, and catalysts were aged at −78 °C)

Catalyst	Ageing time (min)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
					cis-1,4	*trans*-1,4	1,2
$VO(P_{204})_2/$ $Al(i\text{-}Bu)_3$	0	42.4	1.63	4.6	28.0	3.5	68.5
	20	18.7	n.d.[b]	n.d.[b]	26.3	3.4	70.3
	20[a]	9.9	n.d.[b]	n.d.[b]	27.2	3.9	68.9
	30	4.7	1.69	7.1	25.7	3.7	70.6
$VO(P_{204})_2/$ $Al(Oct)_3$	0	66.6	3.76	2.9	31.8	2.6	65.6
	20	28.4	n.d.[b]	n.d.[b]	29.5	3.9	66.6
	20[a]	19.3	2.42	4.5	29.6	5.3	65.1
	30	4.8	2.23	4.1	28.3	3.8	67.9

[a] The catalyst was aged in the presence of a small amount of butadiene monomer ([Bd]/[V] = 10 mol/mol).
[b] n.d. indicates not determined.

Table 5
Variation of polymerization temperature on Bd polymerization with $VO(P_{204})_2/AlR_3$ catalysts in toluene (conditions: [Bd] = 1.85 mol/L, $[V] = 1.85 \times 10^{-3}$ mol/L, [Al]/[V] = 4.0 mol/mol)

Cocatalyst	Temperature (°C)	Time (h)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
						cis-1,4	*trans*-1,4	1,2
$Al(i\text{-}Bu)_3$	−20.0	24.0	34.1	4.01	3.3	21.3	15.9	62.8
	20.0	3.0	31.4	n.d.[a]	n.d.[a]	26.1	9.8	64.1
	40.0	2.0	42.4	1.63	4.6	28.0	3.5	68.5
	70.0	2.0	33.2	1.45	4.8	24.2	4.9	70.9
$Al(Oct)_3$	−20.0	24.0	79.7	5.43	2.7	31.0	8.9	60.1
	20.0	3.0	62.8	n.d.[a]	n.d.[a]	33.2	5.2	61.6
	40.0	2.0	66.6	3.76	2.9	31.8	2.6	65.6
	70.0	2.0	37.7	3.53	3.2	30.9	6.5	62.6

[a] n.d. indicates not determined.

3.4. Polymerization temperatures

The Bd polymerization with V-based catalysts were usually carried out at or below room temperature (20 °C) [4–9] due to unstable active species, which is unfavorable for industrial processes. Thus, to estimate the thermal stability of $VO(P_{204})_2/AlR_3$ (R = *i*-Bu, Oct) catalysts, the influences of the polymerization temperature on the polymerization of Bd were examined and the results are summarized in Table 5. High thermal stability of the two catalysts was found, since the optimal polymerization temperature related to these catalysts turned out at 40 °C; furthermore, a fairly good catalytic activity was also observed even at 70 °C, and the M_n and M_w/M_n ratio seemed independent of polymerization temperature in the range of 40–70 °C.

The superior thermal stability of the oxovanadium phosphonate catalysts to the typical V-based catalyst such as VCl_3 and $VOCl_3$ [5–8] may result from the better stability of V–O–P than that of V–Cl bond as depicted in Fig. 3.

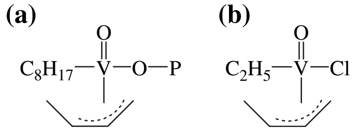

Fig. 3. Structures of active species proposed for oxovanadium phosphonate (a) and $VOCl_3$ (b) catalysts.

Table 6
Variation of polymerization time on Bd polymerization with $VO(P_{204})_2/Al(Oct)_3$ catalyst in toluene at 40 °C (conditions: [Bd] = 1.85 mol/L, [V] = 1.85×10^{-3} mol/L, [Al]/[V] = 4.0 mol/mol)

Time (min)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)		
			cis-1,4	*trans*-1,4	1,2
2	4.23	2.7	31.6	5.0	63.4
5	4.69	2.5	n.d.[a]	n.d.[a]	n.d.[a]
10	5.19	2.5	33.2	2.6	64.2
17	5.02	2.4	31.9	3.7	64.4
120	3.76	2.9	31.8	2.6	65.6

[a] n.d. denotes not determined.

Strong electron donation from phosphonate to the vanadium center accounts for the stability of the active species.

3.5. Kinetic study of the polymerization of Bd with $VO(P_{204})_2/Al(Oct)_3$ catalyst

The polymerization of Bd initiated by $VO(P_{204})_2/Al(Oct)_3$ catalyst with an [Al]/[V] molar ratio of 4.0 was carried out at 40 °C. The results are listed in Table 6 and the plots of the polymer yield and $\ln([Bd]_0/[Bd]_t)$ against time are demonstrated in Fig. 4. A high initial rate was found, within 20 min, the polymer yield increased with time and $\ln([Bd]_0/[Bd]_t)$was proportional to the polymerization time, indicating that the polymerization rate is of the first order with respect to the concentration of monomer. The M_n somewhat tended to decrease with polymerization time while the M_w/M_n ratio fluctuated slightly between 2.4 and 2.9, implying chain transfer became more serious with the polymerization time prolonging.

3.6. Microstructures

The microstructure of resulted poly(Bd) was determined by IR. In the IR spectrum (Fig. 5) of poly(Bd) (sample from line 3 of Table 1), the absorption bands at 732, 909 and 967 cm^{-1} are characteristic of *cis*-1,4, *trans*-1,4 and 1,2-units, respectively, and on the basis of calculation of equations derived by Morero [19], the poly(Bd) is composed of 65.6% of 1,2, 31.8% of *cis* and 2.6% of *trans*-units. The presence of the band at 675 cm^{-1} (for atactic and isotactic-1,2 units) and the absence of the bands at 695, 1111 and 1205 cm^{-1} (only for isotactic-1,2 units) indicate that the configuration of 1,2-units in the sample is atactic [20], and the DSC profile of the sample confirmed an amorphous polymer.

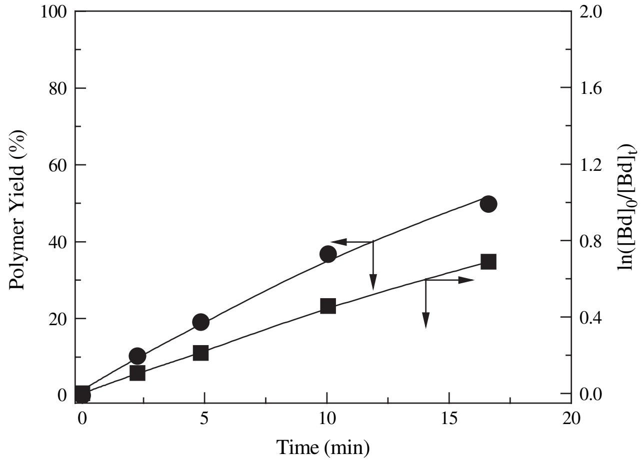

Fig. 4. Plots of the polymer yield (●) and $\ln([Bd]_0/[Bd]_t)$ (■) against polymerization time for Bd polymerization with the catalyst of $VO(P_{204})_2/Al(Oct)_3$. Polymerization conditions: [Bd] = 1.85 mol/L, [V] = 1.85×10^{-3} mol/L, and [Al]/[V] = 4.0 mol/mol in toluene at 40 °C.

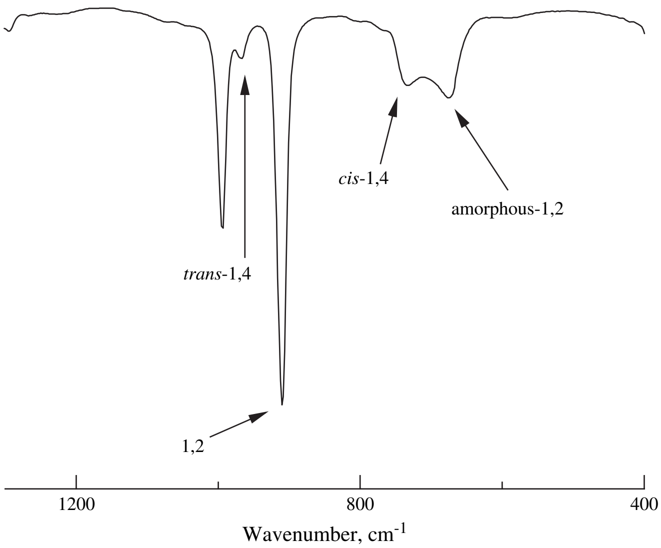

Fig. 5. Infrared spectra of poly(Bd) (sample from line 3 of Table 1; KBr plate).

The microstructures of poly(Bd)s obtained are listed in Tables 1–6. The 1,2-unit content of all the resulted polymers was nearly unchanged with reaction conditions such as [Al]/[V], ageing time, polymerization time, especially that for the $VO(P_{204})_2/Al(Oct)_3$ system, which fluctuated within 5% when reaction temperature was in the range of 40–70 °C. Considering above, an amorphous and high vinyl content poly(Bd) (1,2-units > 65%) was obtained by the $VO(P_{204})_2/Al(Oct)_3$ catalyst, and its high efficiency and stability to polymerization conditions will be practically useful and important.

4. Conclusion

The oxovanadium phosphonates ($VO(P_{204})_2$ and $VO(P_{507})_2$) activated by various alkylaluminums (AlR_3, R = Et, *i*-Bu, *n*-Oct; $HAlR_2$, R = Et, *i*-Bu) were examined in butadiene (Bd) polymerization. As compared with classical vanadium-based catalysts (e.g. $VOCl_3$, $V(acac)_3$), the improvements achieved are summarized as follows: (1) better activity; (2) better thermal sustentation; and (3) microstructure less sensitive to polymerization conditions. Though further improvements are still needed for the practical application of V-based catalyst in Bd polymerization, oxovanadium phosphonate catalysts might give enlightenment on the way of progression.

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