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Polymerization of vinyl ethers using titanium catalysts containing tridentate triamine ligand of the type $N[CH_2CH(Ph)(Ts)N]_2^{2-}$

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ABSTRACT

Titanium complexes having tridentate triamine of the type $N[CH_2CH(Ph)(Ts)N]_2^{2-}$ in combination with methylaluminoxane (MAO) was able to polymerize ethyl vinyl ether in good yields. The polymers obtained in general were having molecular weight in the order of 10^5 with narrow molecular weight distributions. Polymerization conditions had an impact on the molecular weight and the polydispersity index (PDI). Using chlorobenzene as the solvent the polymer had an M_n of 350 000 and PDI of 1.21, where as under neat conditions the M_n was 255 000 with PDI of 1.21. The type of solvent and the temperature dictated the polymerization rate and the polymer stereo regularity. The molecular weight of the polymer is distinctly governed by the polymerization temperature. Temperature ranging between −50 and ambient (30 °C) resulted in high molecular weight polymers and *vice versa* at a temperature of 60–70 °C resulted in low molecular weight polymers in moderate yields. The polymers obtained below 30 °C are highly stereo-regular compared to that of the ones produced at and above ambient temperature. The polymerization of *iso*-butyl vinyl ether (IBVE) was faster than that of linearly substituted *n*-butyl vinyl ether (BVE) and less bulky ethyl vinyl ether (EVE). The order of isotacticities of the polymers obtained are polyIBVE > polyBVE > polyEVE. The use of borate cocatalyst for activation generated narrow molecular weight polymers with a linear increase in the yield and molecular weight over time suggesting the living nature of the catalyst system.

1. Introduction

Utility of metallocene and non-metallocene based early transition metal catalysts in olefin polymerizations are well studied in literature [1]. Identifying the living polymerization of olefins is still the area of interest to many academic and industrial research groups because of their inherent advantage of producing co-polymers containing required repeating units [2]. The utilization of early transition-metal complexes (which behave as Lewis acids) to catalyze the polymerization of electron rich olefins such as vinyl ethers is also well documented in the literature [3]. Recently Masuda and co-workers used metallocene (Fig. 1a) and non-metallocene based titanium complexes (Fig. 1b) in combination with MAO for the polymerization of IBVE, TBVE (*tert*-butyl vinyl ether) and noted that the tacticity of polyVE (polyvinyl ether) was influenced by the catalysts and solvents used [4]. Sawamoto et al. showed stereo-regulation in the cationic polymerization of various alkyl vinyl ethers with bis[(2,6-diisopropyl)phenoxy]titanium dichloride in conjunction with the HCl adduct of IBVE as an initiator in *n*-hexane at −78 °C. Here the tacticity depended on the substituents on monomers, for instance, *iso*-butyl and *iso*-propyl vinyl ethers gave isotactic polymers (mm: 83%), whereas *tert*-butyl and *n*-butyl vinyl ethers resulted in lower isotactic contents (mm: 50%) similar to those for $TiCl_4$, a conventional Lewis acid, thus indicating that the steric bulkiness of the substituents in the monomer was not the critical factor in stereo-regulation. In order to regulate the tacticity of the polymers they have synthesized and employed a series of Lewis acids of the type $TiCl_2(OAr)_2$ as shown in Fig. 1c, in which the metal center carries two substituted phenoxy groups, and a pronounced dependence of isotacticity was observed on the bulkiness, positions, and structure of ring substituents on OAr. Overall, *iso*-propyl groups at 2,6-positions led to the highest isotacticity, whereas bulkier or planar like groups such as *tert*-butyl or phenyl were less effective, suggesting that not only bulkiness but also three-dimensional shapes of Lewis acids are critical in stereo-regulation in cationic polymerization [5]. Yamamoto and Oishi have reported isoselective cationic polymerization of TBVE using variety of aluminum (aryloxide)s with triphenylmethyl fluoride (TrF) initiator and found the relationship between polymer tacticity and counter anion structure, which changed according to the bulkiness,

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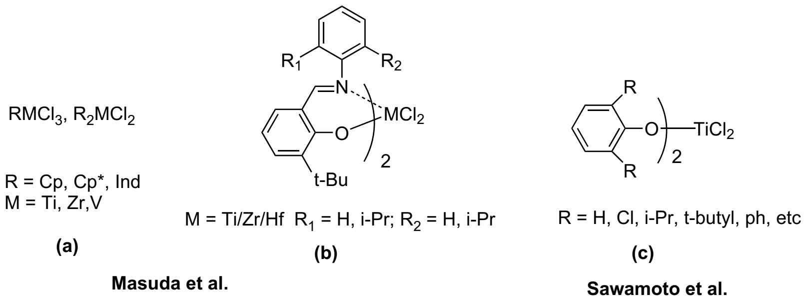


Fig. 1. Few metallocene and non-metallocene catalysts used for vinyl ether polymerization in the literature.

strength and chirality of the Lewis acid combined with TrF so as to make the ionic pair more interactive in the polymerization process [6]. Liu et al. have used a series of cationic palladium complexes as catalysts for the polymerization of vinyl ethers and explained how the ligand donors and cationic nature influence the reactivity of the palladium center in these polymerization reactions [7]. The cationic initiator itself or by generation of cationic initiator upon reaction with the vinyl monomers initiate the polymerization in most of the cases [8]. The carbocationic initiation of vinyl ether is another route to polymerize vinyl ethers as reported by Baird et al. is worth considering in the case of transition metal complexes activated with borate complexes [9].

In our group we have already established the use of aminodiolate and aminotriolate based titanium complexes in combination with aluminum alkyls and MAO for the homo/copolymerization of ethylene, higher α-olefins and cyclic olefins [10]. With these complexes we have established the relationship between the symmetry of catalytically active species and the stereo-regularity of the resulted polyolefins. The use of triamine based titanium complexes is also established from our laboratory for ethylene and higher α-olefins polymerization [11]. In this paper we have demonstrated the ability of these triamine based titanium complexes for the polymerization of vinyl ethers.

2. Experimental section

2.1. General procedures

All manipulations were done under an atmosphere of dry, oxygen-free argon employing vacuum or Schlenk line techniques, unless otherwise noted. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of the polymers were recorded in $CDCl_3$ at an ambient temperature with TMS as the internal standard. ^{13}C NMR spectra of the polymers were recorded with pulse angle = 25°, pulse width = 2.8 μs, acquisition time = 0.655 s, relaxation time = 6 s and number of scans = 3000. Molecular weights of the polymers were determined by Waters GPC instrument with Styragel® columns (10^6, $10^5$and 10^3 Å columns connected in series) equipped with a refractive index (RI) detector using THF as solvent at a flow rate of 1.0 mL/min. Calibration was done using narrow polystyrene standards. Thermal analyses were performed on Stanton Redcrofts simultaneous thermal analyzer (781 series). Toluene was purified by distilling over sodium/benzophenone and degassed with argon. Chlorobenzene and dichloromethane were dried by distilling over CaH_2 and degassed with argon. MAO was purchased as 10% by weight solution from Witco GmbH, Germany and was used after estimating the aluminum content by complexometric titration. Vinyl monomers were purchased from Aldrich Chemical Company and were used as such without further purification.

2.2. Polymerization procedure

To dry deaerated chlorobenzene (10 mL), the precatalyst (1×10^{-6} mol) and MAO in toluene were added by syringe to a clean, dry, argon-filled 100 mL round-bottomed flask equipped with a Teflon® coated magnetic stirrer bar and a septum. The mixture was stirred for about 5 min and then vinyl ether was added and stirring was continued for the required time. The polymerization was quenched by pouring the mixture into a cold methanol solution; the residue was passed through silica gel column with elution of ethyl acetate–chloroform. The desired polymer was obtained upon concentration. All results are summarized in Tables 1–4. The polymers were dried under vacuum and weighed to calculate the activity of catalyst.

2.2.1. Poly(n-butyl vinyl ether)

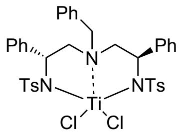
^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.51 (br, 1H, O–CH) 3.41 (br, 2H, O–CH_2), 1.83 (br, 2H, CH_2), 1.52, 1.37 (br, CH_2–CH_2), 0.91 (br, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 75.2 (OCH), 68.1 (OCH_2), 40.5 (CH_2), 33.4, 20.4 (CH_2), 14.8 (CH_3).

3. Results and discussion

The ring-opening reaction of *N*-tosyl-2-phenylaziridine by benzylamine in ethanol at 80 °C resulted in the formation of the bis(*N*-tosyl-2-amino-2-phenylethyl) benzylamine, $[NNN]H_2$. The corresponding titanium complex, $[NNN]TiCl_2$, was prepared by adopting the literature reported procedure (Fig. 2) [11]. It was already established that this catalyst in combination with MAO was able to polymerize ethylene, α-olefins and cyclic olefins. Polymerization of 1-hexene with this catalyst gave high molecular weight polymers with 85% isotacticity at ambient and low temperatures whereas at high temperatures (30–50 °C) it gave oligomers [11].

The polymerization of BVE with the triamine catalysts without co-catalysts yielded oligomers at ambient temperature with very low activity (Table 1, runs 1–3). Increasing or decreasing the temperature did not yield polymers with higher molecular weight nor increase the activity of the catalysts. The polymerization reactions carried out with MAO alone (in the absence of catalysts) did not yield polymers at any instance.

From the literature it is known that some of the metallocene catalysts polymerize vinyl ether upon activation with cocatalysts such as aluminum alkyls or MAO. The polymerization of IBVE and



$[NNN]TiCl_2$

Fig. 2. Catalyst used in this study.

Table 1
Polymerization of BVE in neat conditions using [NNN]TiCl$_2$/MAO.[a]

Run	Al/Ti	BVE (mL)	Time (h)	Yield (%)	M_n/PDI[b]
1	–	3	24	5	1350/1.09
2	–	5	24	3	1600/1.11
3	–	10	24	2	1650/1.12
4	500	5	6	98	255 000/1.41
5	500	50	24	80	180 000/1.52
6	500	5	4	85	212 000/1.34
7	500	5	2	77	156 200/1.32
8	500	5	1	55	70 000/1.25

[a] Reaction conditions: catalyst = 6.92 × 10^{-6} mol except run 5 (6.92 × 10^{-5} mol), Temp. = 30 °C. Runs 1–3, polymerization reactions were carried out without MAO.
[b] From GPC data in THF vs. polystyrene standards.

TBVE with metallocene/MAO catalyst system in toluene afforded stereo-specific polyVE. Several non-metallocene catalysts, including Ti, Zr, and Hf complexes with two phenoxy imine chelate ligands (Fig. 1b), in combination with MAO provided polyIBVE and polyTBVE with 63–68 and 45–51% dyad isotacticity, respectively. These results suggest the tacticity of polyIBVE and polyTBVE was affected by the ligand environment around the catalysts and solvents used [4].

[NNN]TiCl$_2$, in combination with MAO was able to polymerize BVE in good yields (~99% yield in 5–6 h). The polymerization reactions in neat conditions (without any solvent) gave quantitative yields (~100%) same as that of metallocene type catalyst systems. The activity of this catalytic system depended on Al/Ti ratio and in this case, the polymerization activity reached a maximum at an Al/Ti ratio near 500 and then decreased (Fig. 3). The decease in the polymerization activity at higher Al/Ti ratio (>500) is due to more of chain transfer to Al centers in the cocatalyst. The polymers obtained with Al/Ti ratio of 500 is of higher molecular weight than that of the polymers obtained with higher Al/Ti ratio. The results obtained at various conditions are shown in Table 2. The ^{1}H NMR and ^{13}C NMR spectra (Entry 3, Table 2) suggested that the polymers obtained at 30 °C are 35% isotactic (Fig. 4) [4,5]. The amount of isotacticity index increased to 60% when the reaction temperature was lowered to 0 °C and 65% when the temperature was −50 °C. In the ^{13}C NMR spectrum of the polyBVE the –*CH$_2$–CH–O in the back bone appears at 39–42 ppm, –CH$_2$–O in the side chain appears at 72–74 ppm and the –CH$_2$–*CH–O appears at 67–69 ppm. In Fig. 4 we have used the –*CH$_2$–CH–O present in the backbone appearing at 39–42 ppm to calculate the stereo-regularity of the sample. The percentage of *meso* content was independent of the group taken into account for computation. For convenience we have used –*CH$_2$–CH–O in the backbone to calculate the stereo-regularity of all samples.

Table 2
Polymerization of BVE at room temperature.[a]

Catalyst	Run	Catalyst (mg)	Al/Ti	BVE (mL)	Time (h)	Yield (%)	M_n/PDI[b]
[NNN]TiCl$_2$/MAO in chlorobenzene	1	5	100	5	6	52	35 200/1.31
	2	5	200	5	6	62	68 400/1.26
	3	5	300	5	6	95	350 000/1.21
	4	5	400	5	6	74	260 000/1.34
	5	5	600	5	6	60	85 100/1.51
	6	5	1000	5	6	42	55 200/2.01
	7	50	300	50	24	90	272 000/1.24
	8	5	300	5	4	80	268 000/1.19
	9	5	300	5	2	60	209 000/1.16
	10	5	300	5	1	40	144 000/1.14
[NNN]TiCl$_2$/MAO in toluene	11	5	100	5	6	45	18 600/1.82
	12	5	200	5	6	55	72 000/1.72
	13	5	300	5	6	90	250 000/1.12
	14	5	400	5	6	66	124 000/1.91
	15	5	600	5	6	52	42 600/2.12
	16	5	1000	5	6	30	21 000/2.60
	17	50	300	50	24	85	201 000/1.14
	18	5	300	5	4	60	164 000/1.21
	19	5	300	5	2	45	126 000/1.23
	20	5	300	5	1	38	85 000/1.22

[a] Reaction conditions: catalyst = 6.92 × 10^{-6} mol except runs 7, 17 (6.92 × 10^{-5} mol), Temp. = 30 °C.
[b] From GPC data in THF vs. polystyrene standards.

Table 3
Polymerization of BVE in toluene: Yield vs. DP.[a]

Run	Catalyst (mg)	BVE (mL)	Time (h)	M_w/PDI[b]	DP[c]
13	5	5	6	280 000/1.12	2800
18	5	5	4	198 400/1.21	1984
19	5	5	2	155 000/1.23	1550
20	5	5	1	103 700/1.22	1037

[a] Reaction conditions: Catalyst = 6.92 × 10^{-6} mol, Al/Ti = 300, BVE = 5 mL in toluene.
[b] From GPC data in THF vs. polystyrene standards.
[c] Degree of polymerization.

The effect of solvents on the polymerization of BVE using [NNNTiCl$_2$]/MAO system is shown in Table 2. Masuda and coworkers have carried out IBVE and TBVE polymerizations with metallocene and phenoxy imine metal catalysts and reported that the tacticity of polyIBVE and polyTBVE was affected by the catalysts and solvents used. With CpTiCl$_3$/MAO as a catalyst system, highest isotacticities were obtained for polyIBVE (dyad: 72%) and polyTBVE (triad: 42%, dyad: 65%) in *n*-hexane and toluene solvents respectively [4]. When we have carried out the polymerization of BVE using [NNNTiCl$_2$]/MAO catalyst system in solvents such as toluene and chlorobenzene, this catalyst showed better activity at lower Al/Ti ratio (lower MAO content) compared to that of neat conditions suggesting the homogenization of catalytically active species. This homogeneity of the catalytically active species has a direct effect on the rate of the polymerization. The rate of polymerization in chlorobenzene and toluene is comparatively higher than that of neat conditions and non-aromatic solvents such as hexane.

When we carried out the polymerization of BVE in chlorobenzene solvent, we got polymers having very high molecular weight with narrow polydispersity (PDI of 1.2–1.5). The results obtained at various conditions are shown in Table 2 and 3 and the GPC traces are shown in Fig. 5. As we increase the reaction temperature from 30 °C to 50 °C we found a two-fold increase in the activity for the polymerization of BVE. Further increase in temperature led to very low molecular weight polymers with less activity indicating possible decomposition of the catalyst at higher temperature. When the reaction temperature was lowered from 30 °C to 0 °C we got polymers with increased molecular weight but the activity of the catalyst decreased considerably (possibly slow activation of the

Table 4

Comparison of Polymerization of BVE[a] and 1-hexene[b] at different temperatures using [NNN]$TiCl_2$/MAO in chlorobenzene.

Monomers	Temp. (°C)	Time (h)	Yield (%)	M_n (10^{-3})/PDI[c]	% mm[d]
BVE	−50	6	10	–	65
	−10	6	25	–	60
	0	6	30	620/1.17	60
	10	6	35	600/1.16	–
	30	6	95	350/1.21	35
	50	2	98	84/2.54	–
	70	6	25	Oligomers	–
IBVE	30	6	98	410/1.24	75
EVE	30	6	60	284/1.26	61
1-Hexene[e]	−10	48	3.5	50/3.5	70
	−10	24	1.7	36/3.2	70
	0	48	7.3	44/2.6	75
	0	24	5.0	28/2.4	75
	30	48	28.0	21/1.9	82
	30	24	16.8	17/1.8	80
	50	48	57.8	10/1.4	75
	50	24	28.6	8/1.4	75
BVE/1-Hexene[f]	30	6	90 (VE)[g] 05 (H)[g]	210 (PVE) 25 (PH)	–
BVE/$Ph_3CB(C_6F_5)_4$	0	2	90	560/1.12	60
BVE/$Ph_3CB(C_6F_5)_4$	0	1	54	350/1.12	–
BVE/$Ph_3CB(C_6F_5)_4$	0	0.5	26	180/1.12	–

[a] Reaction conditions: Catalyst = 6.92 × 10^{-6} mol, BVE = 5 mL.

[b] Reaction conditions: Catalyst = 2 × 10^{-6} mol, 1-Hexene 5 mL, 20 mL chlorobenzene.

[c] Determined by GPC in THF with narrow polystyrene standards.

[d] Percentage of *mm* diad (PVE) and *mmmm* (polyhexene) pentad determined by ^{13}C NMR spectra.

[e] Results taken from Ref. [11].

[f] 50:50 mixture of vinyl ether and 1-hexene 5 mL.

[g] Determined by GPC in THF.

catalyst at lower temperature). At 30 °C the polyBVE obtained had the maximum molecular weight of 350 000 where as at 0 °C it gave polymers with maximum molecular weight of 600 000 (Table 2). The ^1H NMR and ^{13}C NMR spectra suggested that the polymers obtained at 0 °C were 75% isotactic and the isotacticity index reduced to 65% at ambient temperatures.

Later, we carried out the BVE polymerization in toluene and noted that the trend in polymerization was same as that of chlorobenzene, but the activity was comparatively lower. The optimal Al/Ti ratio was found to be 300. The results obtained at various conditions are shown in Tables 2 and 3. The maximum molecular weight of the polymers obtained at 0 °C was 450 000 and that of 30 °C was 250 000 (Table 2) with narrow PDI. The polymers were isotactic in nature and followed the same trend as that of chlorobenzene based experiments. The maximum isotacticity index obtained at 0 °C was 74%. The polymerization in larger scales also yielded polyBVE with high molecular weight (run: 7; 90% conversion; M_n: 2.72 × 10^5; PDI: 1.24; run: 17; 85% conversion; M_n: 2.01 × 10^5; PDI: 1.14).

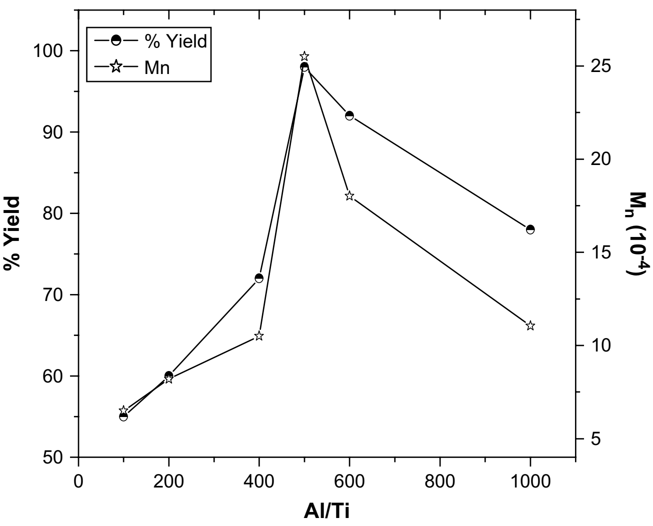


Fig. 3. Trends in polymerization of BVE in neat conditions.

We have also extended our study in-terms of monomer dependence on tacticity of the polymer using two different monomers namely EVE and IBVE. With both the monomers the trends in polymer yield, molecular weight, PDI and other characteristics were same as that of BVE. But the isotacticity indexes were on higher side for polyIBVE and were less for polyEVE in comparison with polyBVE. At room temperature and with chlorobenzene as solvent the polyIBVE had M_n: 4.1 × 10^5; isotacticity index: 75% and that of polyEVE was 2.84 × 10^5; isotacticity index: 61%. The molecular weight and the polymer tacticities increased for low temperature reactions as seen in the case of polyBVE. Presently we are further modifying the ligand environment for better control in polymerization and also exploring the possibility of copolymerization of vinyl ethers because of the excellent properties of the polymers produced [12].

To check whether the polymerization proceeded via coordinate or cationic or carbocationic mechanism we have done three different sets of reactions. Having already demonstrated the ability of these catalysts to initiate 1-hexene polymerization which underwent a quazi-living manner, we have added the mixture of 1-hexene and BVE during the polymerization. To our surprise we have got only polyBVE formation with traces of polyhexene (PH) material. Fig. 6 shows the GPC traces of the obtained polymer, the bi-modal distribution revealed that the polymer was a mixture of two homo polymers. Further chromatographic analysis revealed that the obtained polymer was a mixture of higher molecular weight polyBVE and lower molecular weight PH (Table 4). Based on this observation of forming PH and polyBVE in a single pot we

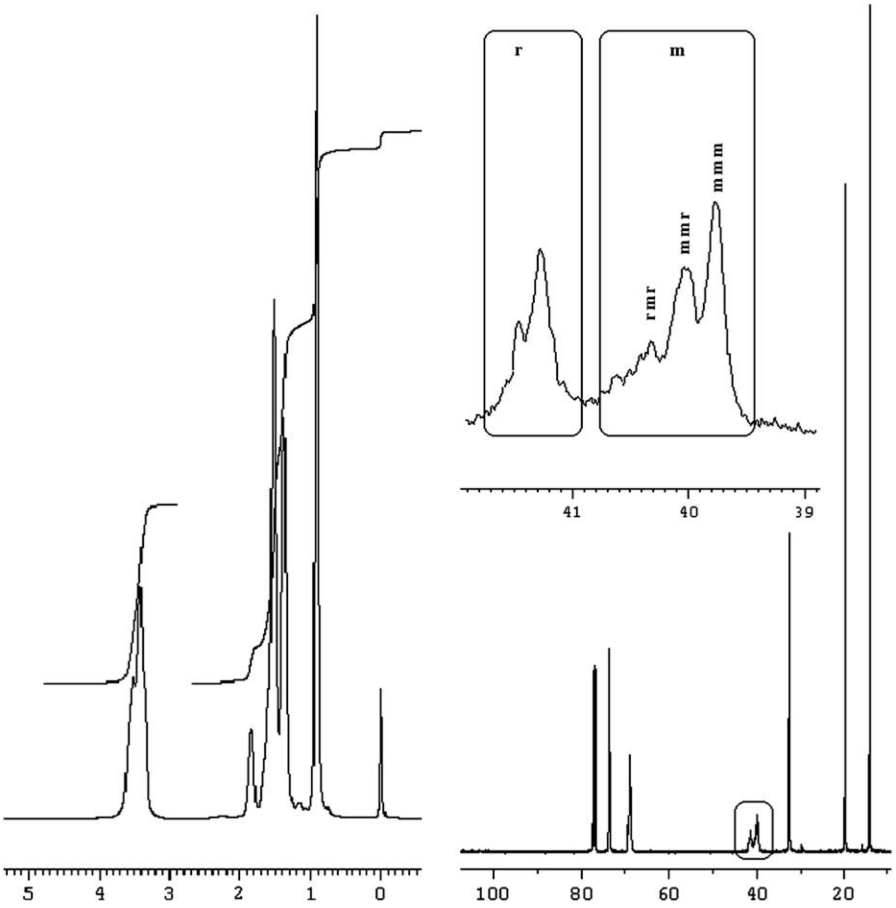


Fig. 4. ^{1}H and ^{13}C NMR spectra of polyBVE (Entry 4, Table 2).

suppose the mechanism of polymerization in both the cases should be different and it may be concluded as a cationic pathway for vinyl ether polymerization as it is commonly accepted and coordination polymerization for the olefin polymerization. The formation of less amount of PH could be related to the reaction rate. Our earlier observation also revealed that the PH formation was slow [11] compared to that of polyBVE. As seen in Table 3 (correlation between polymer yield vs. degree of polymerization (DP)) the molecular weight of the polymer obtained at different time intervals were less than that of the expected molecular weight based on the % conversion. This could be attributed to reactivation of the Ti-polymer bond by excess of MAO to produce fresh cationic species responsible for further chain growth along with the parent one. Apart from MAO we have also used the borate cocatalysts to activate the catalyst and performed vinyl ether polymerization (Table 4). The polymerization with $Ph_3CB(C_6F_5)_4$ approached close to living nature as seen from Table 4. The linear increase in polymer yield, molecular weight with time and the narrow molecular weight dispersion of the polymers obtained revealed the living nature of the catalyst system. The yield obtained after 2 h was 90% and the molecular weight was 560 000 which is close to that of theoretically calculated (M_w (calculated) = 585 000) with PDI of 1.1 supporting living nature of these catalysts. We support the mechanism via carbocationic in the case of borate initiated process as reported by Baird et al. for vinyl ethers and other olefinic polymerization by mono(pentamethylcyclopentadienyl) (C_p^*) complexes of titanium, zirconium, and hafnium [9].

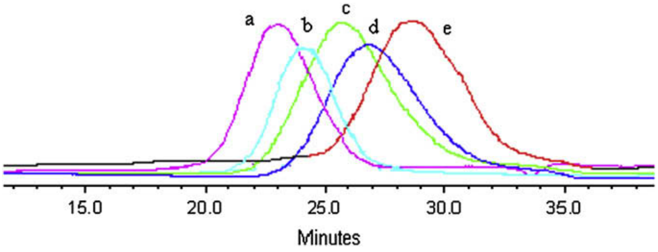


Fig. 5. GPC overlay of polyBVE [Table 2, (a) 13, (b) 17, (c) 18, (d) 19, (e) 20].

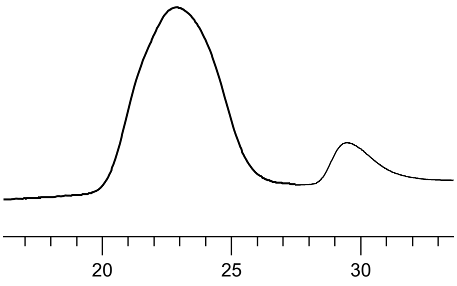


Fig. 6. GPC traces of polymer obtained from the co-polymerization of 1-hexene and BVE using [NNN]$TiCl_2$/MAO catalyst system (Table 4, run 14). The bimodal distribution clearly indicates that the polymerization reaction yielded a mixture of two homo polymers but not a copolymer.

4. Conclusion

The new class of titanatranes containing triamine ligands is a valuable addition to the non-metallocene family which is very effective in vinyl ether polymerization. The triamine based titanium complexes in combination with MAO and borate produced stereoregular high molecular weight polyVE. To our knowledge this is one of the very rare systems which produce narrowly dispersed high molecular weight polyVE at ambient temperatures.

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