Vinyl-Addition Copolymerization of Norbornene and Polar Norbornene Derivatives Using Novel Bis(β-ketoamino)Ni(II)/B(C$_6$F$_5$)$_3$/AlEt$_3$ Catalytic Systems

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ABSTRACT: Copolymerization of norbornene (NBE) and polar norbornene derivatives undergoes vinyl polymerization by using novel catalyst systems formed *in situ* by combining bis(β-ketoamino)Ni(II) complexes {Ni[R$_1$-C(O)CHC(NR$_3$)R$_2$]$_2$ (R$_l$ = R$_2$ = CH$_3$, R$_3$ = naphthyl, **1**; R$_1$ = R$_2$ = CH$_3$, R$_3$ = C$_6$H$_5$, **2**; R$_1$ = C$_6$H$_5$, R$_2$ = CH$_3$, R$_3$ = naphthyl, **3**; R$_l$ = R$_2$ = CH$_3$, R$_3$ = 2, 6-(CH$_3$)$_2$C$_6$H$_3$, **4**; R$_1$ = R$_2$ = CH$_3$, R$_3$ = 2, 6-^{i}Pr$_2$C$_6$H$_3$ **5**; R$_1$ = C$_6$H$_5$, R$_2$ = CH$_3$, R$_3$ = 2, 6-^{i}Pr$_2$C$_6$H$_3$, **6**)} and B(C$_6$F$_5$)$_3$/AlEt$_3$ in toluene. The **1**/B(C$_6$F$_5$)$_3$/AlEt$_3$ catalytic system is effective for copolymerization of NBE with NBE—OCOCH$_3$ and NBE—CH$_2$OH, respectively, and copolymerization activity is followed in the order of NBE—CH$_2$OH > NBE—OCOCH$_3$ > NBE—CN. The molecular weights of the obtained poly-(NBE/NBE—CH$_2$OH) reached 5.97 × 10^4 to 2.07 × 10^5 g/mol and the NBE—CH$_2$OH incorporation ratios reached 7.0– 55.4 mol % by adjusting the comonomer feedstock composition. The copolymerization of NBE and NBE—CH$_2$OH also depend on catalyst structures and activity of catalyst followed in the order of **2 > 1 > 3 > 5 > 4 > 6**. The molecular weights and NBE—CH$_2$OH incorporation ratios of poly(NBE/NBE—CH$_2$OH) were adjustable to be 1.91–5.37 × 10^5 g/mol and 9.5–41.1 mol % —OH units by using catalysts **1–6**. The achieved copolymers were confirmed to be vinyl-addition type, noncrystalline and have good thermal stability (T_d = 380–410°C). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2008–2016, 2011

Key words: norbornene; norbornene polar derivatives; late-transition-metal nickel complexes; vinyl-addition copolymerization

INTRODUCTION

Vinyl addition polymerization of norbornene yields a completely saturated polymer with no rearranged norbornene units. Reviews of routes and catalysts to vinyl addition polymers have recently appeared.[1,2] Vinyl-type polynorbornene (PNBE) exhibits many of the key performance, such as high-thermal stability, very high-glass transition temperature (T_g up to 370°C), high-optical transparency (transmittance > 90% at 400 nm), and low-dielectric constant. Such physical properties are suitable for high-performance polymer material such as nonlinear optical polymers, electroluminescent materials, organic light emitting diodes, photolithographic resist materials, and nanoporous glass matrices for interlayer dielectrics in semiconductors.[3–5] However, pure PNBE exhibits low solubility, mechanical brittleness, poor processability, and insufficient adhesion to substrates with polar surfaces such as silicon, oxides, or metals, which currently are serious disadvantages for the processing of these polymer materials and hinder the application of PNBE, for example, into transparency films and deep ultraviolet photoresist materials.[6] To improve the adhesion and solubility properties and obtain more elastic optical materials holding their characteristic natures, the incorporation of functional groups into PNBE is an efficient method to improve these properties. Recent objectives to improve the properties of PNBE have focused on incorporating pendant functional substituents onto the polycyclic backbone, enabling this class of polymer to be utilized for a wide variety of uses.[7] Successful research of these materials may lead to potential applications in electronic (display) devices.[8] However, the conventional Ziegler-Natta catalysts containing Group 4 transition metal-catalyzed addition polymerization of functional norbornene has proved to be

difficult because of their high oxophilicity, and incorporation of polar monomers has been achieved only after protection of the polar functional groups.[9–11] The less oxophilic character of the late transition metal has been considered to be effective for the polymerization of heteroatom-functionalized monomers.[12] Since norbornene carboxylic acid esters were first polymerized with Pd(II)-based catalysts by Breunig and Risse,[13] subsequent studies on polymerization of other norbornene derivatives containing pendant silyls, carboxyls, amines, sulfonamides, and esters with palladium and nickel catalysts have been described in the literature.[14–24] The use of organo-nickel complexes for the polymerization of norbornene or of substituted functional norbornene monomers has also been described in patent literature.[25–27] Nevertheless, the rate of polymerization of functionalized norbornene is apparently slower than that of the unsubstituted norbornene. More recently, the addition copolymerization of norbornene with functionalized norbornene derivatives has been a particular interesting area.[1,12] Much more significant work has been mainly done by many researchers with palladium complexes.[14,15,19,23,24,28–34] Although the polymerization of norbornene derivatives containing pendant methanol still not reported, the copolymerization of norbornene derivatives containing pendant methanol has been reported. Char and coworkers reported the copolymer of norbornene, 5-ethoxymethyl-2-norbornene, and 5-norbornene-2-methanol by using allylpalladium chloride dimer ([(η^3-allyl)PdCl$_2$] and silver hexafluoroantimonate (AgSbF$_6$) in chlorobenzene.[35] Sen and coworkers reported copolymerization of functionalized norbornene derivatives such as 5-norbornene-2-methanol with ethene using the catalytic systems formed *in situ* by combining Pd(dibenzylideneacetone)$_2$ [Pd(DBA)$_2$] and anionic P-O ligands in a 1 : 1.2M ratio.[36] Owing to the PNBE produced with the Pd-based catalyst generally had a fatal defect that they were poorly dissolved in most organic solvents and result in giving difficulty in processing them after polymerization.[37] Therefore, the Ni(II)-based catalyst is of particular interest because it provides PNBE having excellent processability.[37–39] However, as we known, the copolymerization of norbornene with norbornene polar derivates using nickel compound have only been reported by Suzuki et al.[40] and Wu and coworkers.[41] As for the Ni(II) catalyst, the organoaluminum compound, such as AlEt$_3$ or MAO, has been determined to be an essential ingredient and higher [Al]/[Ni] molar ratios for catalytic activity. Exceptionally, high activity was recently obtained by using salicylaldiminato Ni(II) complex with MAO or MMAO (modified methylaluminoxane) at [Al]/[Ni] = 2000.[42,43] So, it is still important to have a low organoaluminum/metal ratio to reduce industrial operating costs and the amount of cocatalyst residues in the polymer. The latter leads to more advantages for the pro-

spective optical applications of PNBE.[44] It is desirable to find the novel activators, which can be used as substitutes for MAO due to the high production costs of MAO cocatalyst. As a consequence, another possibility to activate late transition metal complexes is to use tris (pentafluorophenyl)borane, [B(C$_6$F$_5$)$_3$], with or without triethylaluminum, [AlEt$_3$].[5,45–51] B(C$_6$F$_5$)$_3$, as a Lewis acid, plausibly plays an important role in the formation of mature active complexes by activating late-transition-metal complexes in the polymerization of NBE. In our previous work, we demonstrated that the well defined, stable, and easily synthesized bis(β-ketoamino)nickel(II) complexes,[52] which activated with a combination of B(C$_6$F$_5$)$_3$, could polymerize norbornene and displayed excellent ability [3.6 $\times$ 10^7 g PNBE/(molNi. h)] and give PNBE with higher yields (up to 90–95%) and high molecular weights ($M_w = 1 \times 10^6$ g/mol).[53] Furthermore, a simple Lewis acid AlEt$_3$ can be applied in the polymerization of norbornene-type monomers as a "third component" and in combination with B(C$_6$F$_5$)$_3$ as a cocatalyst. However, there have been only a few reports that describe the Cp-Ni system, for example, (Cp)Ni(Cl)(PPh$_3$)/AlMe$_3$/B(C$_6$F$_5$)$_3$ can copolymerize norbornene with 5-norbornene-2-carboxylic acid methyl ester in toluene to give higher yields (up to 68% in 2 h at room temperature) and high molecular weights (M_n = 234,100–109,500) and narrow molecular weight distributions (M_w/M_n = 1.78–1.89) of copolymer with variable contents of the methyl ester monomer unit (17.4–60.7 mol %).[54] Insufficient data have been published on the use of Ni(II)-based late-transition metal complexes represent precatalyst and with B(C$_6$F$_5$)$_3$/ AlEt$_3$ as a cocatalyst for vinyl-addition copolymerization of norbornene with functionalized norbornene derivatives. Recently, we also demonstrated that the bis(β-ketonaphthylamino)nickel(II)/B(C$_6$F$_5$)$_3$/AlEt$_3$ can proceed in the efficient copolymerization norbornene-(NBE) with 5-norbornene-2-yl-acetate (NBE—OCOCH$_3$) although exhibited lower catalyst activity for both homopolymerization and copolymerization of NBE-OCOCH$_3$.[55] The promising performance of above catalyst also prompts us to explore the possibility to copolymerize norbornene with different polar norbornene comonomers as well as employment of bis(β-ketoamino)nickel(II) complexes based on different ligand structures for further studies. In this study, the copolymerization behavior and effects of the variation in the polymerization variables, such as employment of different structure catalysts, different polar norbornene derivatives, and comonomers feed ratios, were investigated.

EXPERIMENTAL

General procedure

All manipulations were carried out under an atmosphere of dry and oxygen-free argon using standard

vacuum, schlenk, or under nitrogen atmosphere in glove box (MBraun Co., Munich, Germany). Toluene was dried over sodium/benzophenone and distilled under nitrogen before use. Bis(β-ketoamino)nickel(II)(1–6) complexes {Ni[R_1C(O)CHC(NR_3)R_2]$_2$ (R_l = R_2 = CH_3, R_3 = naphthyl, 1; R_1 = R_2 = CH_3, R_3 = C_6H_5, 2; R_1 = C_6H_5, R_2 = CH_3, R_3 = naphthyl, 3; R_l = R_2 = CH_3, R_3 = 2, 6-$(CH_3)_2C_6H_3$, 4; R_1 = R_2 = CH_3, R_3 = 2, 6-$^iPr_2C_6H_3$ 5; R_1 = C_6H_5, R_2 = CH_3, R_3 = 2, 6-$^iPr_2C_6H_3$, 6)}, which employed here to act as catalysts and activated by $B(C_6F_5)_3$/AlEt$_3$ for the copolymerization of norbornene with polar norbornene derivatives, such as 5-norbornene-2-yl-acetate (NBE-OCOCH$_3$), 5-norbornene-2-yl-methanol (NBE—CH$_2$OH), and 5-norbornene-2-yl-cyano (NBE—CN), were synthesized according to the method reported in our previous work and were dissolved in toluene to make a 5.0×10^{-3} mol/L solution.[53] The tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 95%), Triethylaluminum (AlEt$_3$, 25% wt/wt in hexane, 95%) were used as received. Norbornene (NBE, 99%) were purchased from Alfa Aesar (Massachusetts, USA) and was purified through drying over sodium/potassium and distilled at 110°C under N_2 atmosphere and was dissolved in toluene to make a 0.4 g/mL (0.0425 mol/L) solution. The 5-norbornene-2-yl-acetate (NBE-OCOCH$_3$, 98%, endo/exo = 80/20), 5-norbornene-2-yl-methanol (NBE—CH$_2$OH, 98%), and 5-norbornene-2-yl-cyano (NBE—CN, 98%) was purchased from Aldrich (St. Louis, USA) and used without further purification.

Copolymerization procedure of norbornene and norbornene polar derivatives

The copolymerizations of norbornene and polar norbornene derivatives were carried out in a 100 mL two-necked, round-bottom flask with a magnetic stirring bar and sufficiently purged with nitrogen by using the homogeneous Ni(II) complexes 1–6 precatalyst and with $B(C_6F_5)_3$/AlEt$_3$ as cocatalysts. The appropriate $B(C_6F_5)_3$ solid, and anhydrous toluene, AlEt$_3$, norbornene, norbornene polar derivatives were added sequentially to the reactor, and the copolymerization was conducted at the predetermined temperature by injection of the homogeneous Ni(II) catalyst solution through an injection system with an excess pressure of argon. Temperature was adjusted with a heat jacket connected to a thermostat allowing adjustment of the polymerization temperature with an accuracy of ±0.5°C. The polymerizations were terminated by venting off excess catalyst and addition with 5% HCl/EtOH (vol/vol). The resulting polymer was separated off, washed with fresh methanol, and dried in vacuum at 40°C until the weight remained constant. The total volume of the liquid phase was kept to be 10 mL.

Fractionation procedure

The products, which obtained by copolymerization of norbornene and norbornene polar derivatives using 1–6/$B(C_6F_5)_3$/AlEt$_3$ systems, were fractionated by treating with acetone and cyclohexane solvents because of their solubility differences. A typical procedure: the product mixture was firstly dissolved in acetone to separate the homopolymer of norbornene polar derivative, which is soluble in acetone. Acetone was diffused into product mixture over 24 h while giving a solid and liquid phase. The white solid was collected by filtration and dried under vacuum and then followed by dealing with cyclohexane solvent to further separate the homopolymer of norbornene, which is soluble in cyclohexane. The filtrated solid fraction, which is insoluble in both acetone and cyclohexane solvents, considered to be copolymer of norbornene and norbornene polar derivative fraction still remained to be over 97.2 wt %, whereas the fractions of norbornene polar derivative polymer and norbornene polymer are trace (<2.8 wt %) after the aforementioned fractionation procedure in acetone and cyclohexane.

Characterizations

Fourier transform infrared (FTIR) spectra were measured on a Shimadzu IR Prestige-21 FTIR spectrophotometer with the film method. The ^{1}H-NMR and ^{13}C-NMR spectra of the polymers were recorded on a Bruker ARX 400 NMR spectrometer at room temperature and with chloroform-d and o-$C_6D_4Cl_2$ as solvents for copolymers of NBE and NBE—OCOCH$_3$ and with THF-d as solvents for copolymers of NBE and NBE—CH$_2$OH while tetramethylsilane (d 1/4 130) as an internal reference. Thermogravimetric analysis (TGA) was performed under nitrogen at a heating rate of 10°C/min with a Perkin–Elmer thermogravimetric analyzer TGA 7. The glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 at a heating rate of 10°C/min. The wide-angle X-ray diffraction (WAXD) curves of the polymer powders were obtained using a Bruker D8 Focus X-ray diffractometer, with monochromatic radiation at a wavelength of 1.54 Å. Scanning was performed with 2θ ranging from 3° to 60°. The gel permeation chromatography (GPC) was carried out on a Breeze Waters system consisting of a Rheodyne injector, a 1515 Isocratic pump, a Waters 2414 differential refractometer, and a Styragel column set, Styragel HT3 and HT4 (19 mm × 300 mm, $10^3 + 10^4$ Å), at a flow rate of 1.0 mL/min with chloroform as an eluent, to separate molecular weight (MW) ranging from 10^2 to 10^6. The instrument was calibrated with monodisperse polystyrene standards.

TABLE I
Copolymerizations of Norbornene and Polar Norbornene Derivatives Catalyzed by 1–6/B(C$_6$F$_5$)$_3$/AlEt$_3$ Catalytic Systems[a]

Comonomer	Mol % of polar norbornene derivative in feed-stock composition	Cat.	Conv. (%)	Activity (g/mol Ni·h)	M_w (g/mol)	M_w/M_n	Mol % of polar norbornene derivative in copolymer[b]
NBE—CN	100	1	trace				
NBE—CN	50	1	trace				
NBE—OCOCH$_3$	100	1	3.3	8.36×10^2	1.03×10^4	1.60	100
NBE—OCOCH$_3$	50	1	36.6	7.50×10^3	3.40×10^4	1.85	10.9
NBE—CH$_2$OH	100	1	trace				
NBE—CH$_2$OH	50	1	51.2	1.59×10^4	2.07×10^5	1.23	41.1
NBE—CH$_2$OH	50	2	56.9	2.07×10^4	2.89×10^5	1.69	9.5
NBE—CH$_2$OH	50	3	45.5	1.84×10^4	5.37×10^5	1.51	–
NBE—CH$_2$OH	50	4	18.4	6.70×10^3	2.73×10^5	1.78	–
NBE—CH$_2$OH	50	5	43.9	1.65×10^4	3.19×10^5	1.24	22.7
NBE—CH$_2$OH	50	6	10.8	3.93×10^3	1.91×10^5	1.27	–
NBE—CH$_2$OH	0	1	23.1	3.60×10^3	0.38×10^4	2.10	0
NBE—CH$_2$OH	10	1	93.6	3.03×10^4	1.26×10^5	2.58	trace
NBE—CH$_2$OH	30	1	63.3	2.17×10^4	1.59×10^5	1.28	7.0
NBE—CH$_2$OH	50	1	51.2	1.59×10^4	2.07×10^5	1.23	41.1
NBE—CH$_2$OH	70	1	13.5	5.18×10^3	5.97×10^4	1.21	55.4
NBE—CH$_2$OH	90	1	trace	n.d	n.d	n.d	n.d

[a] Conditions: C$_{[Cat.]}$= 5×10^{-4} mol/L; t_p = 12 h; T_p = 60°C; $n_{[NBE]} + n_{[NBE—OCOCH_3 \text{ or NBE—CH}_2\text{OH or NBE—CN}]}$ = 1 mol; $n_{[Al]}/n_{[B]}/n_{[Cat.]}$ = 1500/20/1; Solvent: toluene; V_p = 10 mL; n.d.: not detectable.
[b] Incorporated polar norbornene derivative content in copolymer, which was a rough relative estimated by ^{13}C-NMR measurement.

RESULTS AND DISCUSSION

Influences of different comonomers on copolymerization

The results that copolymerization of norbornene and NBE—OCOCH$_3$ were effect carried out with 1/B(C$_6$F$_5$)$_3$/AlEt$_3$,[55] which leads us to focus on copolymerization norbornene with different polar norbornene comonomers as well as employment of nickel(II) complexes 1–6 based on different ligand structures for further studies. In an effort to investigate whether 1/B(C$_6$F$_5$)$_3$/AlEt$_3$ could copolymerize norbornene and polar norbornene derivatives, a series of copolymerization were carried out with norbornene and polar norbornene derivatives comonomers like NBE—CH$_2$OH, NBE—OCOCH$_3$, and NBE—CN. The copolymerization results of norbornene and polar norbornene derivatives were summarized in Table I. The 1/B(C$_6$F$_5$)$_3$/AlEt$_3$ catalytic systems did not result in any activity for either polymerization or copolymerization of NBE—CN while exhibited lower catalyst activity for both polymerization and copolymerization of NBE—OCOCH$_3$. However, higher activity exhibited for copolymerization of NBE and NBE—CH$_2$OH although almost showed no activity for NBE—CH$_2$OH homopolymerization. The copolymerization activity in the order of NBE—CH$_2$OH > NBE—OCOCH$_3$ > NBE—CN indicated that —CN is more hazard to the active species. These results can be explained by the higher polar of the —CN substituted on the 5-position of norbornene, which possess the alone electronic and higher coordination ability to the active center, and plays a role in lowering nucleophility of the polar monomer.

Influences of different catalysts on copolymerization

As seen in Table I, the copolymerization activities of NBE and NBE—CH$_2$OH were significantly affected by different catalyst structure. Comparing the activities of catalysts 1, 2, 3, 4, 5, and 6 at the same reaction conditions, it can be found that the activities of complex 2 is apparently higher than other complexes and followed in the order of 2 > 1 > 3 > 5 > 4 > 6. This fact indicates that the active species loss rate depends on the nickel complexes, and a close relationship between structure–activity of these nickel complexes. Compared with the steric effect, Ni(II) complex 2 with the unique steric effect phenyl ring substituent connected with the imino group seem to play an important role in stabilizing the active species generated from the reaction between the Ni complex precursors and B(C$_6$F$_5$)$_3$/AlEt$_3$. Compared with the electron effect, Ni(II) complexes 1 and 3 with the chelating naphthyl ring has more steric bulk but a stronger electronic conjugation over a wider range, which reduces the electron cloud
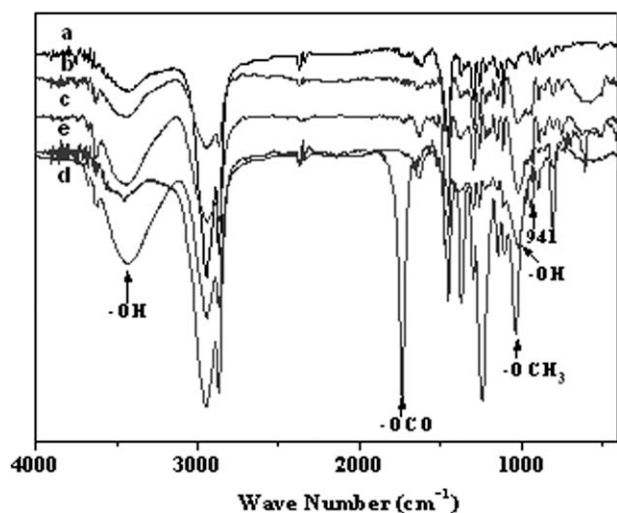
Figure 1 FTIR spectra for (a) polynorbornene; for poly(NBE/NBE—CH$_2$OH) with (b) 7.0%, (c) 41.1%, and (d) 55.4% NBE—CH$_2$OH; and (e) 10.9% NBE—OCOCH$_3$ in poly(NBE/NBE—OCOCH$_3$) obtained by **1**/B(C$_6$F$_5$)$_3$/AlEt$_3$ system.

density of Ni^{2+} (active species) and weakens Ni—C bond, and thus is also favorable to the coordination of monomer to Ni^{2+} active species.

The obtained poly(NBE/NBE—CH$_2$OH) is soluble in THF and has good solubility in chloroform after esterification, and the molecular weights of poly(NBE/NBE—CH$_2$OH) were indirectly determined via esterification. Both molecular weights and NBE—CH$_2$OH incorporation ratio depend on the different catalyst structure and were adjustable to be 1.91–5.37 × 10^5 g/mol, whereas the NBE—CH$_2$OH incorporation rate were 9.5–41.1 mol % —OH units by using catalysts **1**–**6**.

Influences of different comonomers feed ratios on copolymerization

As seen in Table I, the **1**/B(C$_6$F$_5$)$_3$/AlEt$_3$ system has higher catalyst activity for copolymerization of norbornene with NBE—CH$_2$OH, and slight addition of NBE—CH$_2$OH in the feedstock composition gives rise to significant increase of catalyst activity. Nevertheless, the activity of catalyst decreased with redundant increase of the NBE—CH$_2$OH due to coordination of the functional group to metal center consequently deactivating the catalyst. The molecular weights of copolymers reached 5.97 × 10^4–2.07 × 10^5 g/mol, whereas the NBE—CH$_2$OH incorporation ratio depends on the NBE—CH$_2$OH content and were adjustable to be 7.0–55.4 mol % —OH units at a NBE—CH$_2$OH content of 30–70 mol % in the feedstock composition. The lower NBE—CH$_2$OH content may come from lower polymerization rate of NBE—CH$_2$OH.

FTIR spectra of the copolymers

The FTIR spectra of the obtained copolymers by **1**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ with 10.9 mol % of NBE—OCOCH$_3$ and 7.0–55.4 mol % NBE—CH$_2$OH incorporation units in poly(NBE/NBE—CH$_2$OH) at a NBE—CH$_2$OH content of 30–70 mol % in the feedstock composition are present in Figure 1 and of the obtained poly(NBE/NBE—CH$_2$OH) catalyzed by different **1**–**6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems are present in Figure 2. The absence of the vibration bands of carbon–carbon double bond at 1620–1680 cm^{-1} revealed the characteristic signals of the copolymers. As expected, the FTIR spectra of the copolymers show typical bands of vinyl-type addition copolymers, the characteristic absorption peak signals at about 941 cm^{-1} could be attributed to the ring of bicyclo[2.2.1]heptane, as noted by Kennedy and Makowski.[56] There are no absorptions at about 960 cm^{-1}, which would be assigned to the characteristic trans form of stretching of the C=C double bond of the ROMP structure of PNBE.[57] The characteristic signal of the carbonyl group (C=O) at 1735 cm^{-1} and —OH group at 3432 cm^{-1} were clear. These results indicate that the catalytic systems can efficiently copolymerize NBE with NBE—OCOCH$_3$ and NBE—CH$_2$OH, respectively, and the copolymerization occur via a vinyl-type (2,3-linked) addition polymerization mechanism rather than a ROMP mechanism. Moreover, the characteristic signal of the —OH group at 3432 cm^{-1} show an increase in the intensity of the bands related to its —OH with the NBE—CH$_2$OH content increase in the feedstock composition. This indicated that increasing NBE—CH$_2$OH content in the feed increased its incorporation into the copolymer.
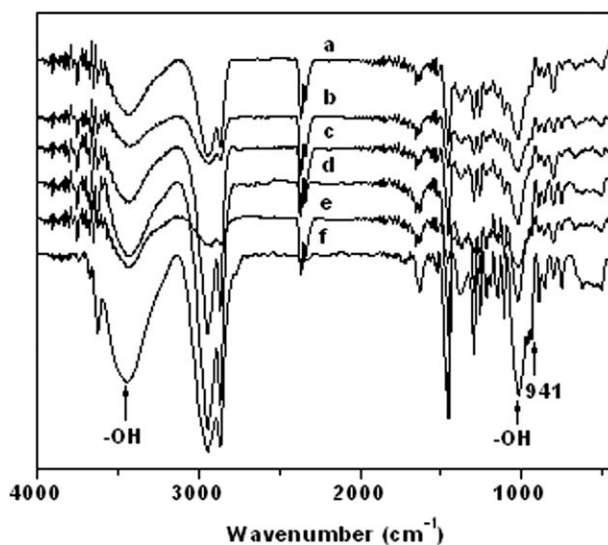

Figure 2 FTIR spectra of the obtained poly(NBE/NBE—CH$_2$OH) catalyzed by different **1**–**6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems, (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

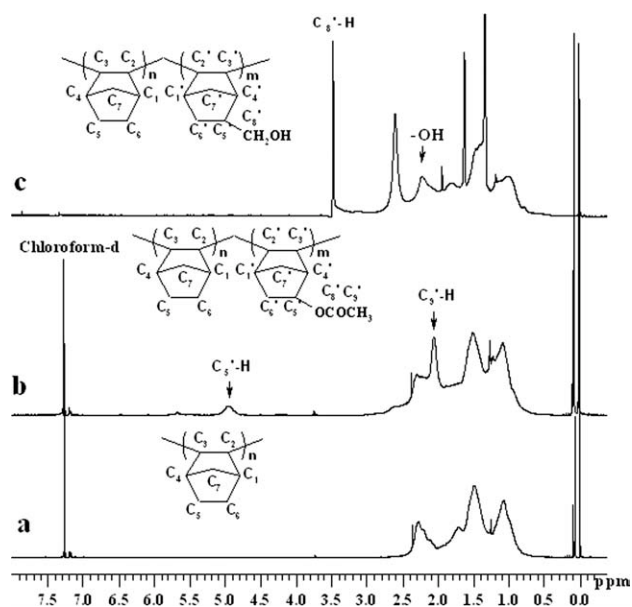**Figure 3** ^{1}H-NMR spectra of copolymers obtained by $1/B(C_6F_5)_3/AlEt_3$ system. (a) polynorbornene, (b) with 10.9% NBE—OCOCH$_3$ in poly(NBE/NBE—OCOCH$_3$), and (c) with 41.1% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH).

^{1}H and ^{13}C-NMR spectra of the copolymers

The ^{1}H-NMR spectra of copolymers obtained by $1/B(C_6F_5)_3/AlEt_3$ with 10.9 mol % NBE—OCOCH$_3$ in poly(NBE/NBE—OCOCH$_3$) and 41.1 mol % NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) are present in Figure 3 and of the obtained poly(NBE/NBE—CH$_2$OH) catalyzed by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems are present in Figure 4. The copolymers were a vinyl addition in nature since both of polynorbornene and copolymers show the resonance absence of the proton connected to the double bond at about 5.0–6.0 ppm.[39,58] The ^{1}H-NMR spectra also show the characteristic signal of —OCOCH$_3$ proton region at about 2.0 ppm (C$_{9'}$—H) and aromatic region at 4.8 ppm (C$_{5'}$—H), whereas the —CH$_2$OH proton region at about 3.49 ppm (—CH$_2$—) and 2.2 ppm (—OH).[35,36]

As shown in the ^{13}C-NMR spectra with 10.9 mol % NBE—OCOCH$_3$ in poly(NBE/NBE—OCOCH$_3$) and 41.1 mol % NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) obtained by $1/B(C_6F_5)_3/AlEt_3$ (Fig. 5) and of poly(NBE/NBE—CH$_2$OH) obtained by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems (Fig. 6), five groups carbon atoms resonances (30.3–31.5 ppm), (35.6–37.7 ppm), (38.8, 39.8, and 42.8 ppm), (47.9, 48.3, and 50.9 ppm), and 172.0 (m, CO) ppm were observed in ^{13}C-NMR spectra of the poly(NBE/NBE—OCOCH$_3$), whereas several groups carbon atoms resonances (29.4–30.8 ppm, C$_5$/C$_6$, C$_{6'}$), (34.6–37.0 ppm, C$_7$/C$_{7'}$), (38.6–42.9 ppm, C$_{1'}$/C$_{5'}$/C$_4$/C$_{4'}$), (45.9–47.0 ppm, C$_1$/C$_{2'}$/C$_2$), (47.0–50.0 ppm, C$_3$/C$_{3'}$), and (62.9–63.0 ppm, —CH$_2$—, labeled as C$_{8'}$) were observed in ^{13}C-NMR spectra of the poly(NBE/NBE—CH$_2$OH).
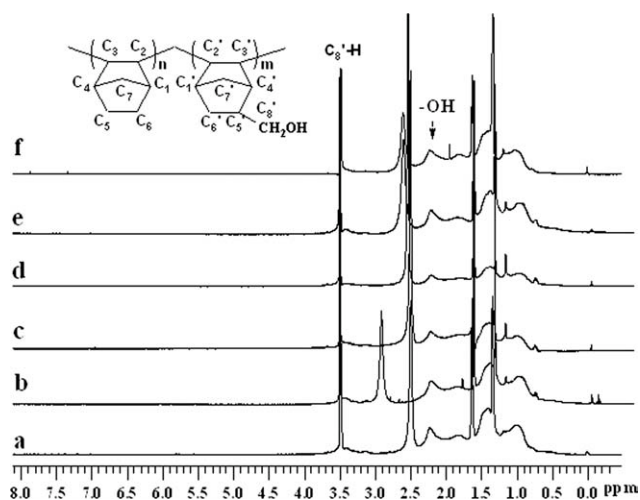
Figure 4 ^{1}H-NMR spectra of the obtained poly(NBE/NBE—CH$_2$OH) catalyzed by different **1–6**/B(C$_6$F$_5$)$_3$/AlEt$_3$ systems. (a) **6**, (b) **5** (22.7%), (c) **4**, (d) **3**, (e) **2** (9.5%), and (f) **1** (41.4%).

The results further confirmed that copolymerization of NBE with both NBE—OCOCH$_3$ and NBE—CH$_2$OH by above catalyst system occurred without ring opening but via a 2,3 addition of the different monomers.

TGA and DSC analyses of the copolymer

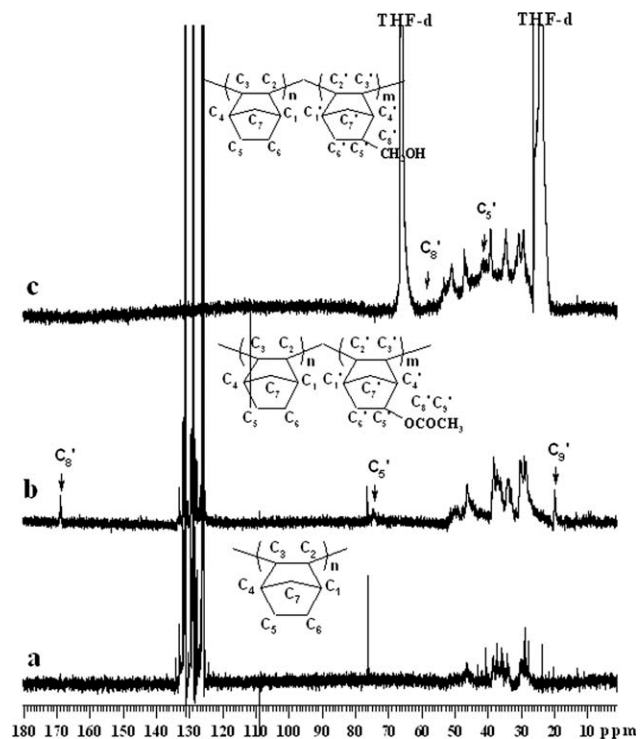As can be seen from the TGA curves of poly(NBE/NBE—CH$_2$OH) with different NBE—CH$_2$OH content

Figure 5 ^{13}C-NMR spectra of copolymers obtained by $1/B(C_6F_5)_3/AlEt_3$ system. (a) polynorbornene, (b) with 10.9% NBE—OCOCH$_3$ in poly(NBE/NBE—OCOCH$_3$), and (c) with 41.1% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH).
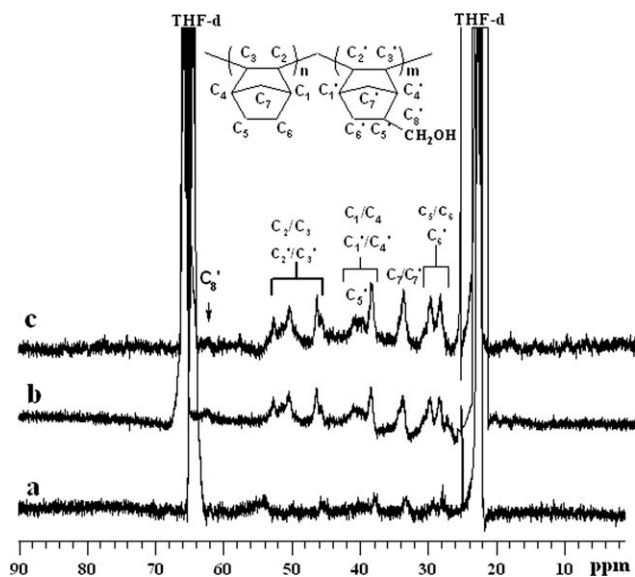
Figure 6 The ^{13}C-NMR spectra of the obtained poly (NBE/NBE—CH$_2$OH) catalyzed by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems. (a) with 9.5% NBE—CH$_2$OH in poly (NBE/NBE—CH$_2$OH) obtained by **2**, (b) with 22.7% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) obtained by **5**, and (c) with 41.1% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) obtained by **1**.

prepared by **1**/B(C$_6$F$_5$)$_3$/AlEt$_3$ (Fig. 7) and of poly (NBE/NBE—CH$_2$OH) obtained by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems (Fig. 8), the thermal stability of all copolymers is similar, and decomposes start to occur at high temperatures from 380 to 410°C. The glass transition temperatures (T_g) of the copolymers were also investigated by DSC analyses. However, efforts to observe the glass transitions temperature over 300°C failed.
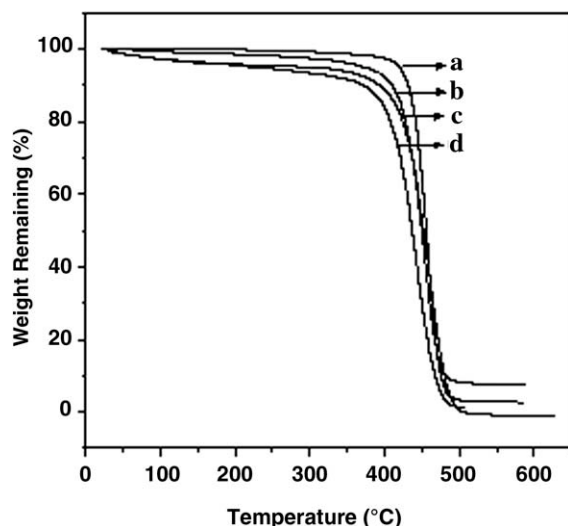

Figure 7 TGA curves for (a) polynorbornene; (b) 7%, (c) 41.1%, and (d) 55.4% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) obtained by **1**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems.
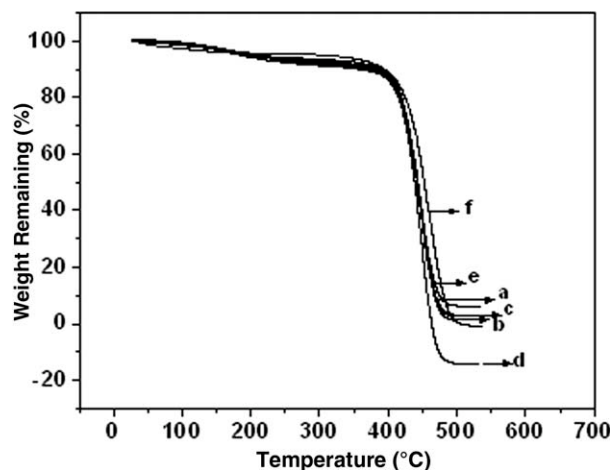
Figure 8 TGA curves of poly(NBE/NBE—CH$_2$OH) obtained by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems, (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

WAXD of the copolymer

The powder wide-angle X-ray diffraction (WAXD) patterns of poly(NBE/NBE—CH$_2$OH) with different NBE—CH$_2$OH content prepared by **1**/B(C$_6$F$_5$)$_3$/AlEt$_3$ are present in Figure 9 and that of obtained poly (NBE/NBE—CH$_2$OH) by different **1–6**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems are present in Figure 10. Two broad halos at 2θ values of 10.44° and 18.45° were observed. The occurrence of two halos is characteristic for PNBE and the corresponding distances amount to 8.46 Å and 4.75 Å.[59] No traces of Bragg reflections, characteristic of crystalline regions, are revealed, and the polymers are therefore noncrystalline. The packing of the copolymers changes little when the incorporated NBE—CH$_2$OH is only 0.66 mol %, but when the incorporated NBE—CH$_2$OH content is more than 7.0 mol %, the intensity of both
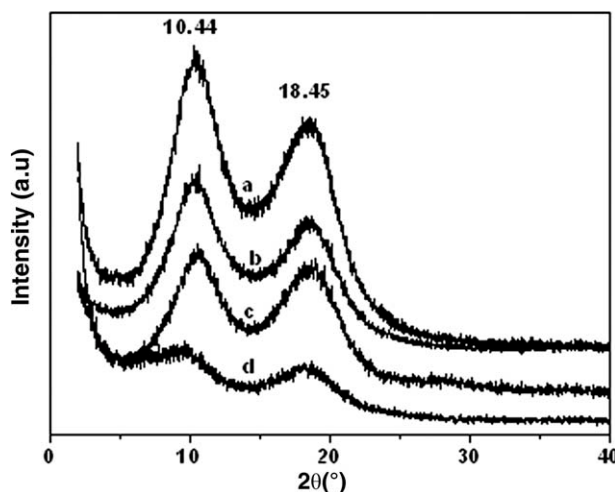

Figure 9 WAXD curves for (a) polynorbornene; (b) 7%, (c) 41.1%, and (d) 55.4% NBE—CH$_2$OH in poly(NBE/NBE—CH$_2$OH) obtained by **1**/B(C$_6$F$_5$)$_3$/Al(Et)$_3$ systems.
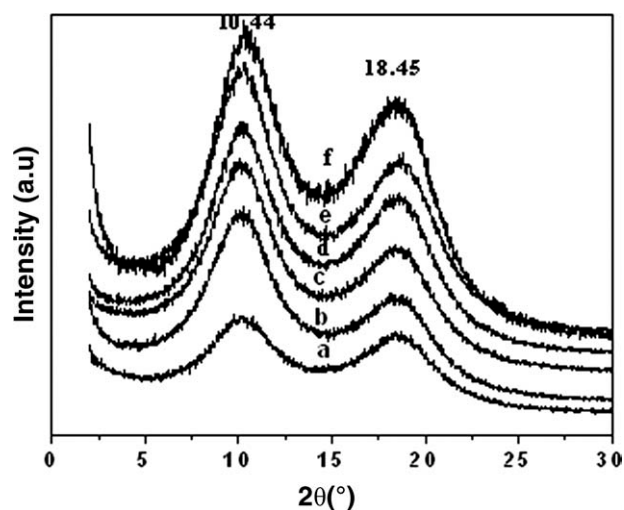
Figure 10 WAXD curves of poly(NBE/NBE—CH₂OH) obtained by different **1–6**/B(C₆F₅)₃/Al(Et)₃ systems, (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

halos become weaker with the increase of NBE—CH₂OH content. This also shows that the NBE—CH₂OH monomers have incorporated to the polymer backbone and the packing density is decreased relative to PNBE through the copolymerization of NBE and NBE—CH₂OH.

CONCLUSIONS

The investigated **1–6**/B(C₆F₅)₃/AlEt₃ demonstrate to be an efficient catalysts systems for the copolymerization of NBE with NBE—OCOCH₃ andNBE—CH₂OH, respectively, and exhibit higher catalyst activity for copolymerization of NBE with NBE—CH₂OH and to yield vinyl-addition type and noncrystalline poly(NBE/NBE—CH₂OH) with high molecular weights. Slight addition of NBE polar derivatives in copolymerization of NBE and NBE polar derivatives gives rise to significant increase of catalyst activity. However, redundant increase of the NBE polar derivatives content in the feedstock composition resulted in decrease of catalyst activity. The incorporation ratio of NBE—CH₂OH in poly(NBE/NBE—CH₂OH) reached 7.0–55.4 mol % by adjusting monomer feedstock compositions and 9.5–41.1 mol % adjustable by choice different catalyst structures.

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