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Homopolymerization and Copolymerization of *tert*-Butyl Methacrylate and Norbornene with Nickel-Based Methylaluminoxane Catalysts

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ABSTRACT: The homopolymerization and copolymerization of *tert*-butyl methacrylate (tBMA) and norbornene (NB) with nickel(II) acetylacetonate in combination with methylaluminoxane were systematically investigated. This catalytic system showed high activity toward the homopolymerization of both NB and tBMA. For these copolymerizations, activity was gradually lost with an addition of tBMA to NB or of NB to tBMA. This result was qualitatively explained with the trigger coordination mechanism. Furthermore, the determination of the reactivity ratios indicated a significantly higher reactivity for NB than for tBMA ($r_{\text{NB}} = 4.14$

and $r_{\text{tBMA}} = 0.097$), and this was interpreted by the coordination mechanism. The synthesized acrylate/NB copolymers exhibited glass-transition temperatures of 100–250°C. The absence of crystallinity and the homogeneous repartition of the monomer units along the main chain yielded products with high transparency and high stability © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1824–1833, 2004

Key words: polynorbornene; metallocene; methylaluminoxane (MAO)

INTRODUCTION

Norbornene (NB) and its derivatives can be polymerized through ring-opening metathesis polymerization,^{1,2} cationic polymerization,³ and olefin addition polymerization. In the last case, the bicyclic structure of the monomer is retained. Depending on the catalytic system used, different polynorbornenes (PNBs) may be obtained, ranging from amorphous ones to more stereoregular and crystalline ones.^{4–6} Molecular dynamic simulations have shown that PNBs display a characteristic rigid random-coil conformation and restricted rotation around the main chain.^{7,8} According to their peculiar structure, these polymers exhibit very high decomposition temperature, high thermal stability, excellent dielectric properties, and unusual transport properties. Therefore, they are attractive materials not only for microelectronics and optical applications⁷ but also for other potential applications in packing and gas separation.⁹

However, the PNB homopolymer presents some disadvantages: it is a very brittle material at room temperature, and its solubility in common organic solvents is rather low. In addition, the processability

of the homopolymer is very poor. Therefore, to improve the processability, researchers have investigated the copolymerization of NB with other traditional vinyl monomers such as ethylene. Through the addition of these monomer units to the polymer chain, the solubility of the polymers in common organic solvents can be increased.

The polymerization of NB can be achieved with some selected catalyst systems based on metallocenes^{6,10,11} or Pd(II) and Ni(II) complexes.^{4,5,7–9,12–14} Metallocene-based systems lead to a stereospecific homopolymer, but the monomer conversion rate is rather low. However, palladium catalysts usually give amorphous polymers.

The use of organo-nickel complexes for the polymerization of NB or substituted functional NB monomers has been described in the patent literature.^{15–17} Recently, it has also been reported that nickel-based methylaluminoxane (MAO) catalysts can polymerize NB with acrylate, diene, NB, and styrene monomers.^{18–26} The polymerization of NB with this type of catalyst system has also been mentioned in Japanese patents,^{27,28} but no details have been given.

In this article, we report a preliminary study of the homopolymerization and copolymerization of NB with *tert*-butyl methacrylate (tBMA) in the presence of nickel(II) acetylacetonate [Ni(acac)₂] associated with an MAO catalyst system. The thermal properties of the produced copolymer are also presented in detail.

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EXPERIMENTAL

Materials

Toluene, Ni(acac)₂, NB, and tBMA with a purity of 99% were supplied by Aldrich Chemical Co. (Milwaukee, WI). NB and tBMA were distilled under reduced pressure before use. Ni(acac)₂ was used without further purification. Toluene was distilled twice over sodium/benzophenone before use. MAO (10 wt % in toluene) was used as received.

Polymerization

The polymerization was carried out under dry nitrogen in toluene at room temperature in a glass flask equipped with a rubber septum. Ni(acac)₂ was first dissolved in the reaction solvent, and MAO was then added. After 15 min for the activation of the catalytic system, the monomers were finally introduced to initiate the polymerization. After a given reaction time, the polymerization mixture was poured into a large amount of methanol containing a few percent of hydrochloric acid to precipitate the polymer. The liquid phase was filtered, and the recovered polymer was dried *in vacuo*. The percentage of the polymer yield was calculated as the weight function of the converted monomer over the total monomer as follows:

Yield (%) =

$$\frac{\text{Weight of resulting polymer}}{\text{Weight of total monomers}} \times 100\% \quad (1)$$

The catalytic activity was defined as the weight of the resulting polymer divided by the amount of introduced Ni(II) and the polymerization time (h):

Catalytic activity =

$$\frac{\text{Weight of resulting polymer}}{\text{Weight}_{\text{Ni(II)}} \times \text{Time}_{\text{polymerization}}} \quad (2)$$

Characterization

The thermal properties were measured with a TA Instrument 2920 differential scanning calorimeter (USA) with a mechanical cooling accessory. Each sample was first heated to 250°C and was kept at that temperature for 5 min. It was then quickly quenched to 30°C. The glass-transition temperature (*T_g*) was obtained as the inflection point of the jump heat capacity with a scanning rate of 20°C/min and within a temperature range of 30–200°C. IR spectra of copolymer films were determined with the conventional NaCl disk method. The film used in this study was sufficiently thin to obey the Beer-Lambert law. Fourier transform infrared (FTIR) measurements were re-

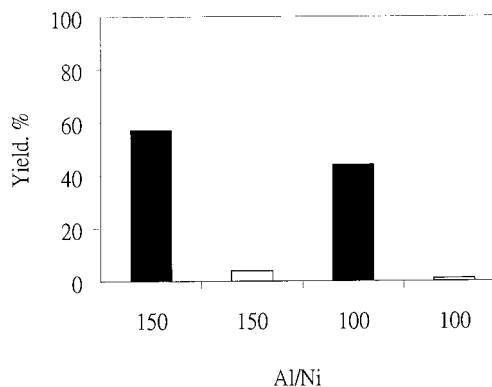


Figure 1 Yield of NB polymerization ([NB] = 7.4 mol/L, polymerization time = 4 h, temperature = 0°C, and [Ni] = 0.0016 mol/L): (■) Ni(acac)₂/MAO and (□) MAO alone.

corded on a Nicolet Avatar 320 FTIR spectrophotometer (USA), and 32 scans were collected with a spectral resolution of 1 cm⁻¹. ¹³C and ¹H spectra were recorded on a Varian spectrometer (USA) and a Bruker AC300 spectrometer (Germany) in C₆D₆, and high-resolution solid-state ¹³C-NMR experiments were carried out at room temperature with a Bruker DSX-400 spectrometer operating at resonance frequencies of 399.53 and 100.47 MHz for ¹H and ¹³C, respectively. The ¹³C cross-polarization/magic-angle spinning (CP-MAS) spectra were measured with a 3.9-μs 90° pulse, with a 3-s pulse delay time, an acquisition time of 30 ms, and 2048 scans. All NMR spectra were taken at 300 K with broad-band proton decoupling and a normal cross-polarization pulse sequence. A magic-angle-sample spinning rate of 5.4 kHz was used to avoid absorption overlapping.

RESULTS AND DISCUSSION

Polymer syntheses

The polymerization activity of Ziegler-Natta and metallocene catalysts depends on several parameters, such as the aluminum/transition-metal ratio, the polymerization temperature, the transition-metal/monomer ratio, and the monomer composition. In this study, we investigated how these parameters could affect the activity of the Ni(acac)₂/MAO catalytic system in the homopolymerization and copolymerization of NB with tBMA.

Influence of the catalyst system

Preliminary experiments were made to check the polymerization activity of each component. The Ni(acac)₂ catalyst alone in the absence of MAO was inactive for the NB and tBMA polymerization, and MAO alone was able to initiate the NB polymerization with very low activity. Furthermore, in a previous study by

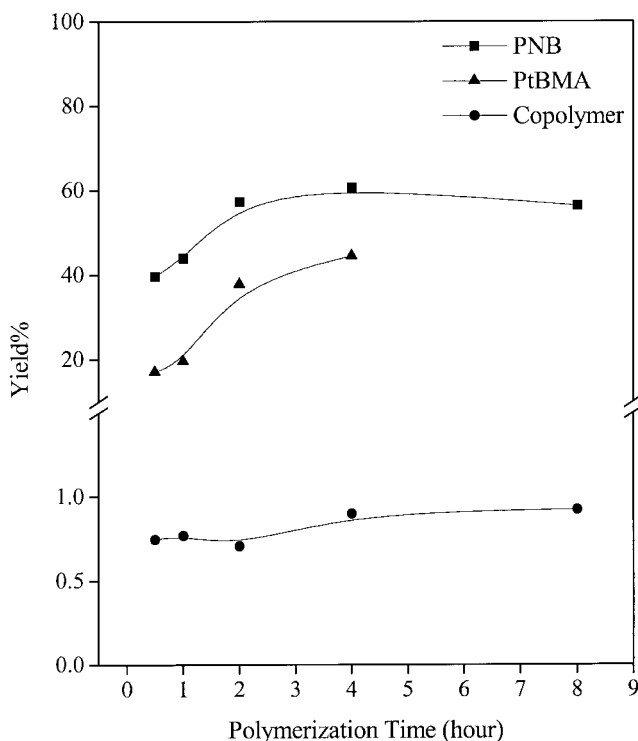


Figure 2 Dependence of the yield on the polymerization time (composition feed ratio of the tBMA/NB copolymer = 0.41/0.58, $[\text{Ni}] = 0.0016 \text{ mol/L}$, $\text{Al/Ni} = 100$, and temperature = 0°C).

Endo et al.,¹⁸ MAO alone was unable to polymerize with tBMA because of the cationic mechanism. Figure 1 shows that the polymer yield obtained in the presence of MAO alone was substantially lower than that obtained in the $\text{Ni}(\text{acac})_2/\text{MAO}$ system. This result reveals that the combination of $\text{Ni}(\text{acac})_2$ and MAO is essential in this catalytic system and that the active centers are formed through interactions between these two components.

Influence of the polymerization time

Figure 2 displays the influence of the polymerization time on the yield for both homopolymerization and copolymerization. For homopolymerization, the polymer yield increased as the time increased, and two distinct periods could be observed in the polymerization process. In the first period of 0–2 h, there was a rapid increase of the yield with the time. In the second period (ca. 2 h), the polymer yield increased only slightly or approached a constant value. For copolymerization, the overall activity was relatively lower at 0.75% after 0.5 h and remained unchanged thereafter.

Influence of the polymerization temperature

A series of polymerization runs were performed at temperatures ranging from 0 to 40°C while other pa-

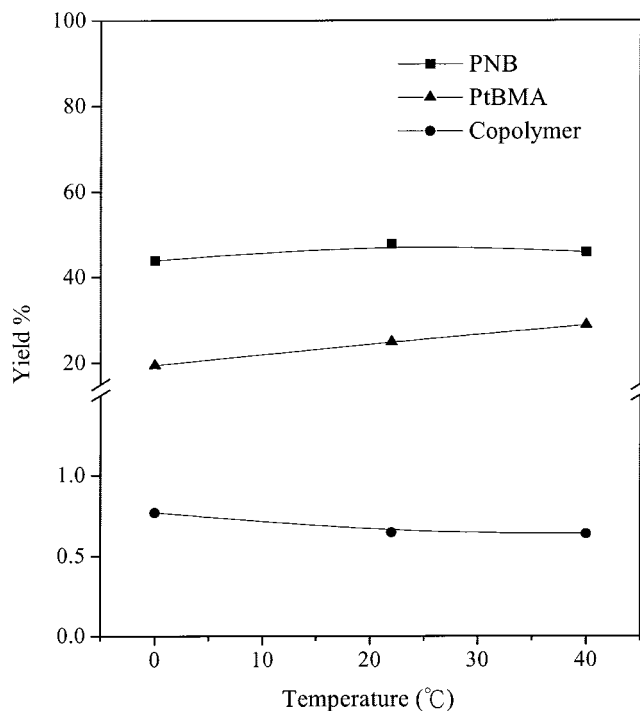


Figure 3 Dependence of the yield on the polymerization temperature (composition feed ratio of the tBMA/NB copolymer = 0.41/0.58, $[\text{Ni}] = 0.0016 \text{ mol/L}$, $\text{Al/Ni} = 100$, and time = 1 h).

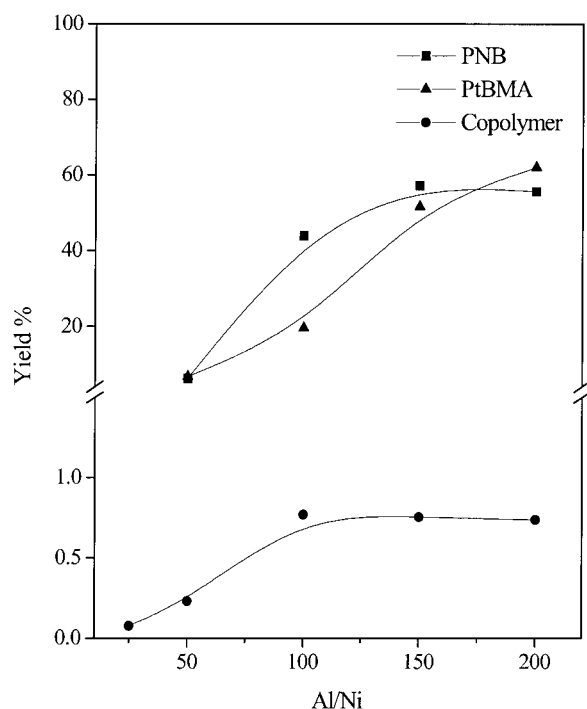


Figure 4 Dependence of the yield on the Al/Ni ratio (composition feed ratio of the tBMA/NB copolymer = 0.41/0.58, $[\text{Ni}] = 0.0016 \text{ mol/L}$, temperature = 0°C , and time = 1 h).

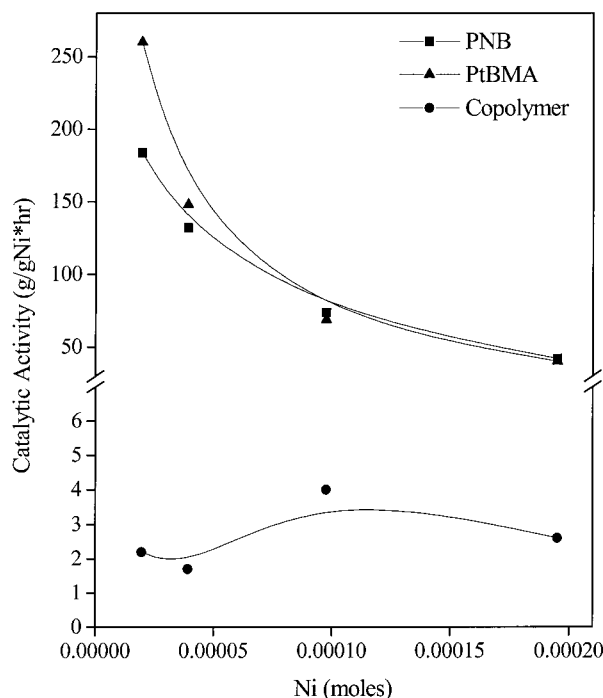


Figure 5 Catalyst activity versus the moles of nickel (composition feed ratio of the tBMA/NB copolymer = 0.41/0.58, amount of Al = 0.01 mol, temperature = 0°C, and time = 1 h).

rameters were kept constant. Figure 3 shows no significant effects of the temperature on the polymer yield or catalyst activity for both homopolymerization and copolymerization.

Influence of the Al/Ni ratio

The dependence of the polymerization yield on the Al/Ni molar ratio is shown in Figure 4. The observed behavior for both homopolymerization and copolymerization is common to many Ziegler–Natta and metallocene systems, the catalytic activity increasing initially and then remaining nearly constant. These results can be interpreted as an increasing number of active species. At a certain higher Al/Ni molar ratio, it approached its maximum concentration of active species. In the case of NB homopolymerization, the maximum yield was obtained at a relatively lower Al/Ni ratio of about 150. For the tBMA homopolymerization, a slightly higher Al/Ni ratio (>200) was necessary to obtain the maximum yield. Despite the higher yield obtained in the homopolymerization reactions (55% for NB and 60% for tBMA), it was surprising to find that the maximum yield of the copolymerization of NB and tBMA, at the same high Al/Ni ratio (>200), was only at 0.74%.

Influence of the moles of nickel

Figure 5 shows the dependence of the catalytic activity on the moles of nickel. For both NB and tBMA ho-

mopolymerizations, an exponential decrease in the activity with the moles of nickel was observed. The activity of the copolymerization of NB and tBMA was extremely low but seemed to be independent of the nickel concentration.

Influence of the monomer composition

A series of copolymerization reactions were performed with different feed compositions while other parameters were kept constant, such as the Al/Ni ratio, moles of nickel, temperature, and time. Figure 6 shows the dependence of the polymerization yield on the initial feed composition. For comparison, the yields of the homopolymerizations are also presented. Increasing the initial tBMA feed led to a drastic decrease in the product yield of the copolymer with respect to the NB homopolymerization. However, despite the high activity observed for the tBMA homopolymerization, a low content of NB (12%) in the initial feed caused it to lose nearly all its activity in comparison with the tBMA homopolymerization. This peculiar behavior of the $\text{Ni}(\text{acac})_2/\text{MAO}$ system in the NB/tBMA copolymerization is discussed later.

Polymer characterizations

^{13}C -NMR spectroscopy was used to characterize the structures and compositions of the homopolymers and copolymers. The spectra obtained for the ho-

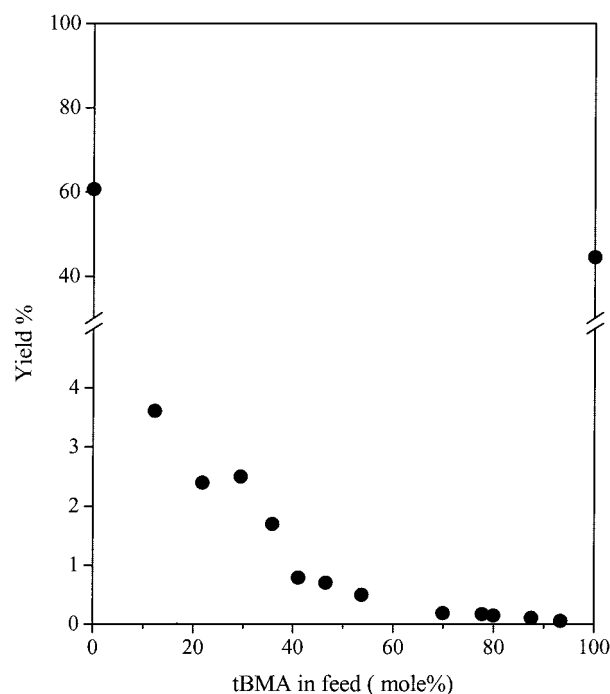


Figure 6 Influence of the composition of the feed on the yield ($[\text{Ni}] = 0.0016 \text{ mol/L}$, Al/Ni = 100, temperature = 0°C, and time = 4 h).

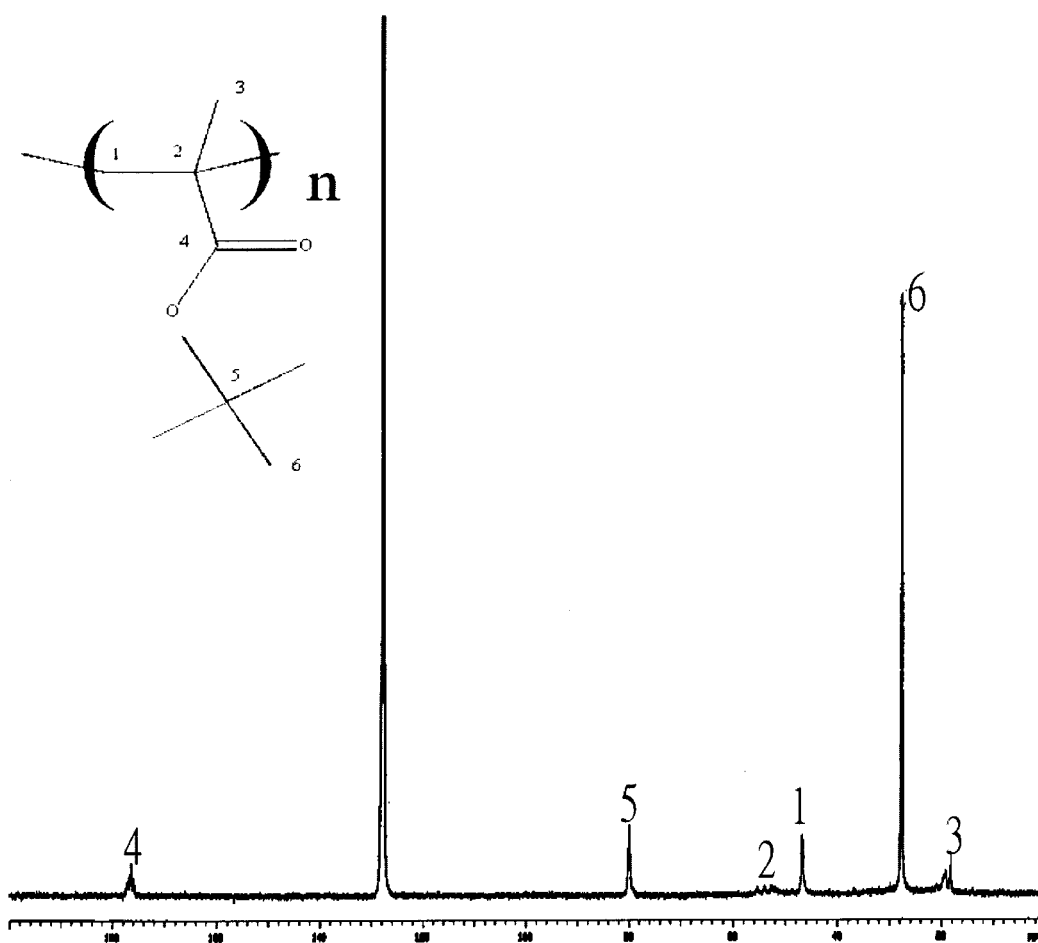


Figure 7 Liquid-state ^{13}C -NMR spectrum of PtBMA in C_6D_6 .

mopolymer of tBMA are shown in Figure 7, and the peak assignments have been reported previously.^{29–33} Solid-state ^{13}C -NMR was used to compare the two homopolymers and the copolymer of NB and tBMA because PNB is insoluble in most organic solvents. Figure 8 shows the major peaks of PNB between 20 and 60 ppm, which are essentially the same as those reported in the literature.^{29,30,34} These results indicate that the polymerization of NB with the $\text{Ni}(\text{acac})_2/\text{MAO}$ system occurred without ring opening and via 2,3-addition. As shown in Figure 8, the obtained copolymer included major peaks from these homopolymers. However, the carbonyl peak of tBMA (176.6 ppm) in the copolymer shifted to a higher field than pure poly(*tert*-butyl methacrylate) (PtBMA; 171.1 ppm). It is well known that the chemical shift strongly depends on the chemical environment of neighboring molecules and conformation packing.³⁵ In general, a chemical shift to a higher field implies that the carbonyl group of tBMA is in a diluent segment. In light of the chemical structure of PNB, the nonpolar group of PNB may act as an inert diluent segment for the carbonyl group of tBMA. If PNB and PtBMA were physically mixed, we would not expect any chemical

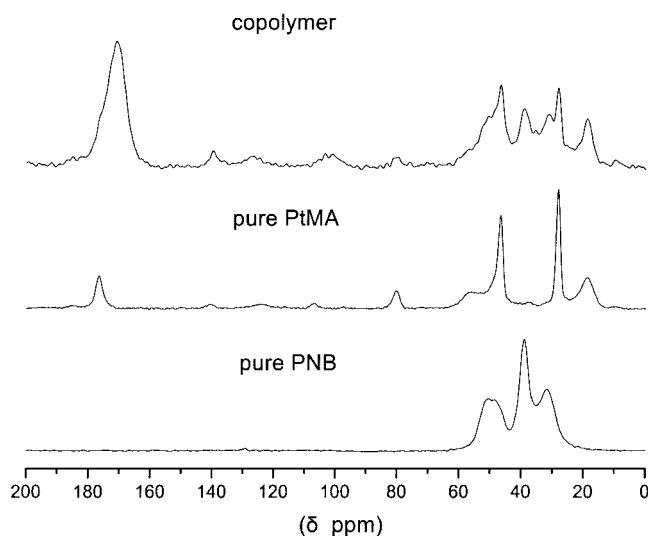


Figure 8 CP-MAS solid-state ^{13}C -NMR spectra of PNB, PtBMA, and the NB/tBMA copolymer with a feed ratio of 0.2/0.8.

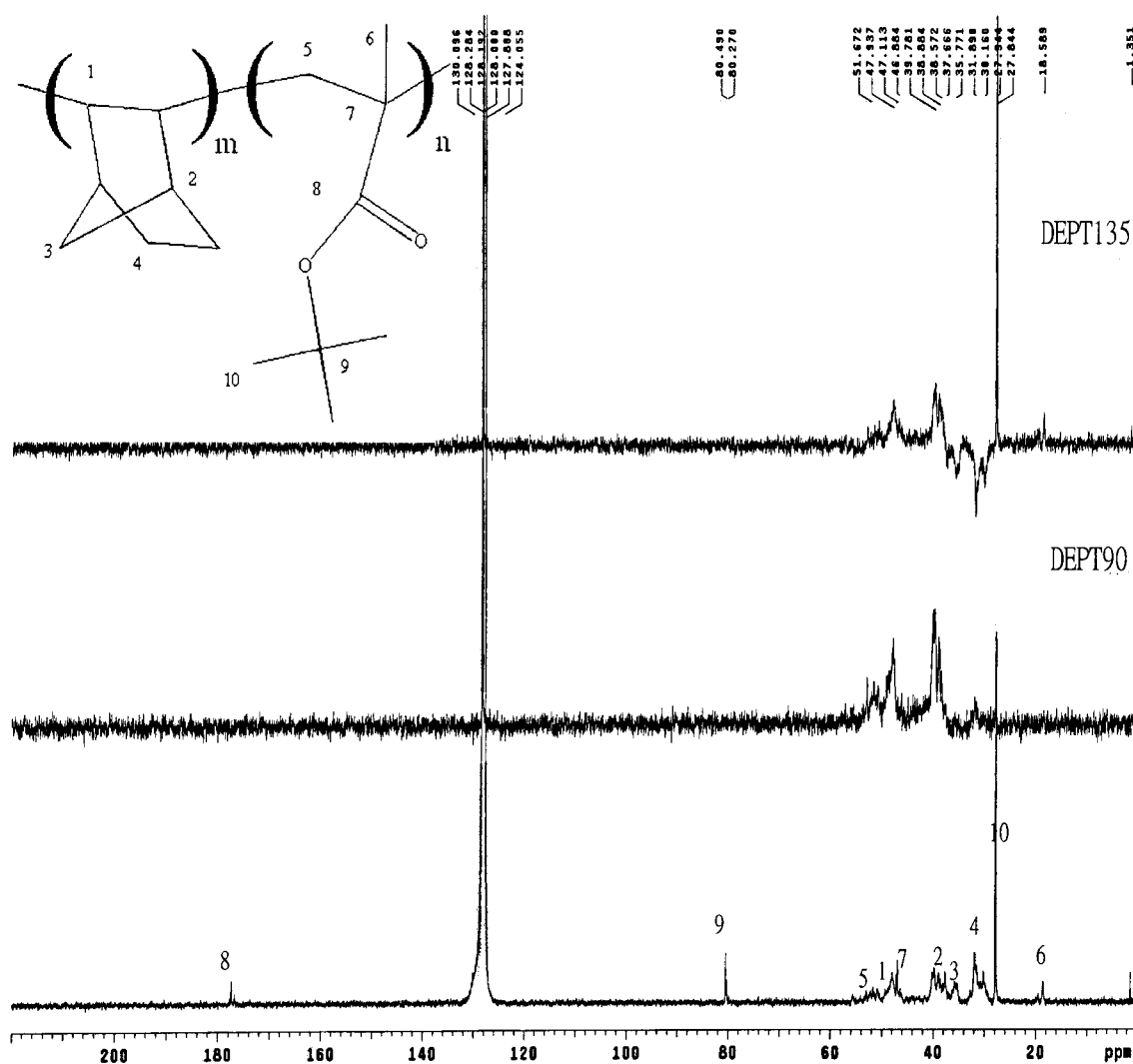


Figure 9 Liquid-state ^{13}C -NMR DEPT spectrum of the NB/tBMA copolymer with a feed ratio of 0.2/0.8.

shift of the tBMA carbonyl because of no specific interaction between these two polymers. In Figure 9, the liquid ^{13}C -NMR and distortionless-enhancement-by-polarization-transfer (DEPT) techniques have been used to assign peaks appearing in the spectrum of the copolymer. All these peaks have been labeled according to the structure of the two monomer units in the polymer chain. The characteristic peak from the $\text{C}=\text{C}$ double bond is absent from the spectrum, whereas the four usual groups of resonances (1–4 labeled peaks) appear.^{29,30} This means that the copolymerization of NB and tBMA with the $\text{Ni}(\text{acac})_2/\text{MAO}$ catalyst system took place without ring opening and via an addition polymerization.

The proportions of these two monomers in the copolymer prepared at a low conversion were determined through an analysis of these peak areas. The molar fractions of the copolymer were determined through these well-resolved peaks. For example, the molar fraction of tBMA in the NB/tBMA copolymer

was determined from the C10 peak of tBMA and the C3 peak of NB.

The variation of the copolymer composition determined by ^{13}C -NMR versus the copolymer feed is shown in Figure 10, which indicates that the incorporation of tBMA into the copolymer chain was substantially slower than that of NB. In addition, the IR spectrum of Figure 11 shows the same trend: the carbonyl group of tBMA decreased as NB increased in the feed. The reactivity ratios determined by the Kelen-Tüdös^{36,37} method were $r_{\text{tBMA}} = 0.097$ and $r_{\text{NB}} = 4.14$ (Fig. 12); they implied that NB had significantly higher reactivity than tBMA. These observed reactivity ratios were rather unusual, clearly not agreeing with a free-radical or cationic polymerization mechanism but instead supporting a coordination-type mechanism. The mechanism is discussed in detail later.

The T_g values of the tBMA and NB homopolymers and the corresponding copolymers were measured with differential scanning calorimetry (DSC). Figure

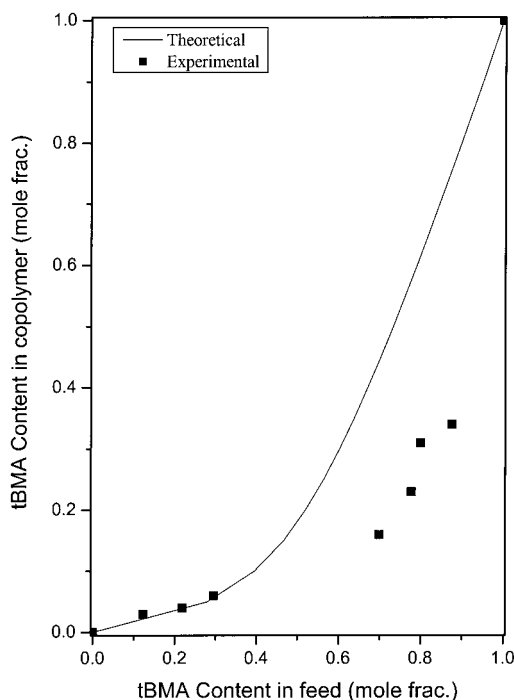


Figure 10 Influence of the monomer feed on the tBMA/NB copolymer composition. The theoretical line represents the prediction by the Kelen-Tudos method.

13 shows that the T_g values of pure PtBMA and PNB were 104 and 230°C, respectively.³⁸ A single T_g was observed for the copolymer (NB feed ratio = 30%) at 134°C.

The thermogravimetric analysis (TGA) thermograms for the PtBMA and PNB homopolymers and the tBMA/NB copolymers are shown in Figure 14(a,b). PtBMA showed three weight losses, whereas only a one-step weight loss was found for pure PNB. The first-step and second-step weight losses of pure PtBMA, at 250 and 400°C, were due to anhydride bond formation between adjacent groups for PtBMA and main-chain decomposition, respectively. The third-step weight loss at 500°C was due to the decomposition of the anhydride bond.^{33,37} The observed one-step weight loss of pure PNB at 450°C was due to the decomposition of the main chain. For the tBMA/NB copolymer, three-step decomposition occurred at 250, 425, and 500°C; this was the same as for their respective homopolymers, as shown in Figure 14(a). In Figure 14, we can see the same tendency of the copolymer compositions determined by NMR and IR spectroscopy. The extent of weight loss at 250°C of the copolymer decreased with an increase in the NB constant, as expected. Meanwhile, the extent of weight loss at 425°C increased with the increase in the NB content because of the decrease in the tBMA fraction and the increase in the NB content in the copolymer chain.

Polymerization with nickel-based catalysts can precede by a coordination mechanism.¹⁵ In fact, the ^{13}C -

NMR spectra of PNB revealed that the polymerization of NB with the $\text{Ni}(\text{acac})_2/\text{MAO}$ system occurred without ring opening and via 2,3-addition; this was similar to a previous study.¹⁶ The 2,3-addition mode is characteristic of a coordination mechanism. On the contrary, radical or cationic polymerization leads to 2,7-addition.³ In addition, the reactivity ratios determined by the Kelen-Tudos method were significantly higher for NB ($r_{\text{NB}} = 4.14$) than for tBMA ($r_{\text{tBMA}} = 0.097$). It is well known that the observed reactivity ratio in free-radical polymerization is in reverse order ($r_{\text{tBMA}} \gg r_{\text{NB}}$). This result suggests that a coordination mechanism is involved in this $\text{Ni}(\text{acac})_2/\text{MAO}$ system. On the basis of this mechanism, we can assume that the interaction between the nickel complex and MAO produces a cationic center. In the absence of the monomer, MAO and nickel centers closely interact and lead to lower activity. In the presence of monomers, a σ - π bond complex is involved in the cationic nickel center and results in higher reactivity. These complexed monomers are inserted between the alkyl group and the nickel center. The repetition of the complexation-insertion step leads to polymer chain growth and is terminated through β elimination of the hydrogen atom. It is well known that chain termination and transfer reactions can proceed through β elimination of the hydrogen atom from the last inserted α olefin.³⁹ In contrast, the β elimination of hydrogen would be much more difficult for the last inserted NB because of the strain effect of the cycloring, which is thermodynamically unfavorable. This result can explain the reactivity ratio of NB being much higher than that of tBMA in copolymerization.

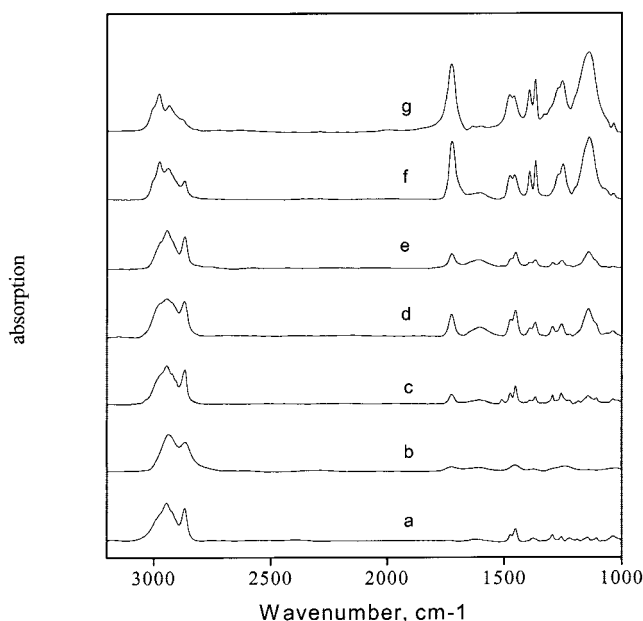


Figure 11 FTIR spectra of the polymers synthesized with the following NB/tBMA feed ratios: (a) 100/0, (b) 87/13, (c) 64/36, (d) 58/42, (e) 53/47, (f) 22/78, and (g) 0/100.

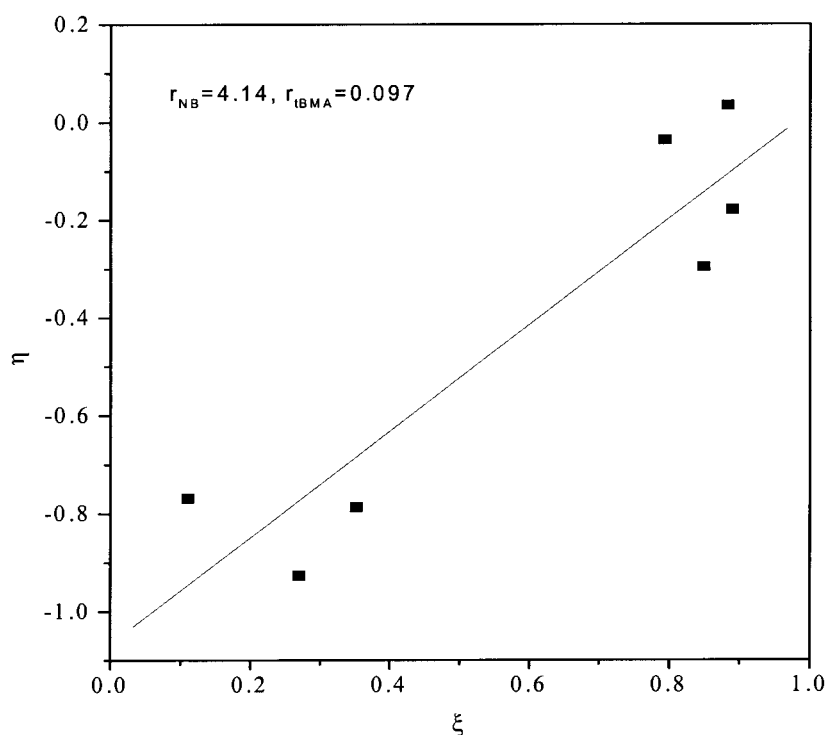


Figure 12 Plot for the Kelen-Tudos method.

Nevertheless, some results are difficult to explain by the coordination mechanism. A very low content of NB in the initial feed (12 mol %) led to a drastic loss of activity in comparison with tBMA homopolymeriza-

tion, whereas a gradual loss of activity with respect to NB homopolymerization was observed in the presence of a significant amount of tBMA (Figs. 6 and 10). This peculiar behavior can be interpreted in a qualita-

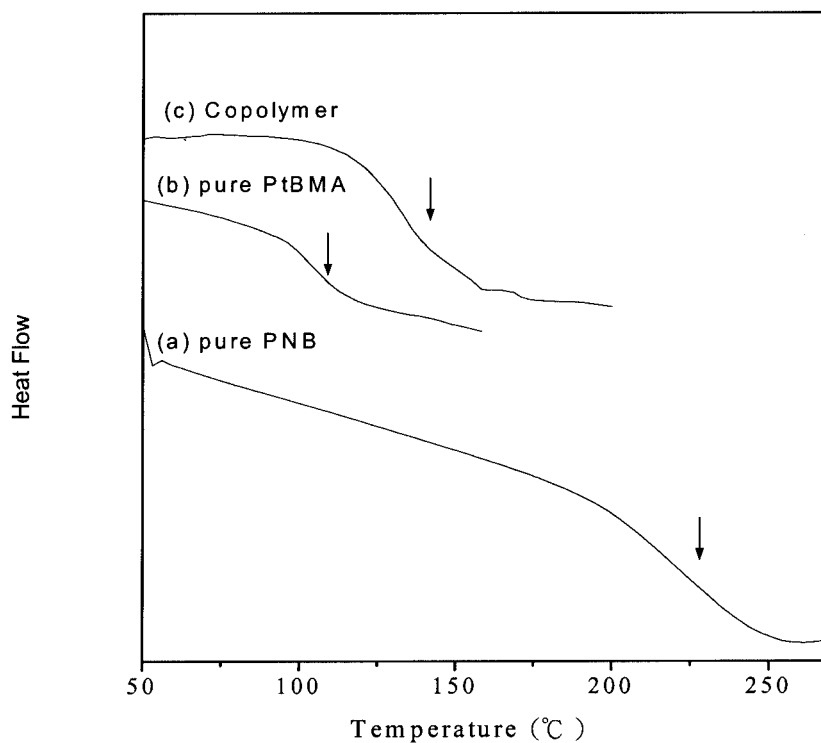


Figure 13 DSC thermograms for the homopolymers and copolymer. The NB/tBMA feed ratio for the copolymer was 0.3/0.7.

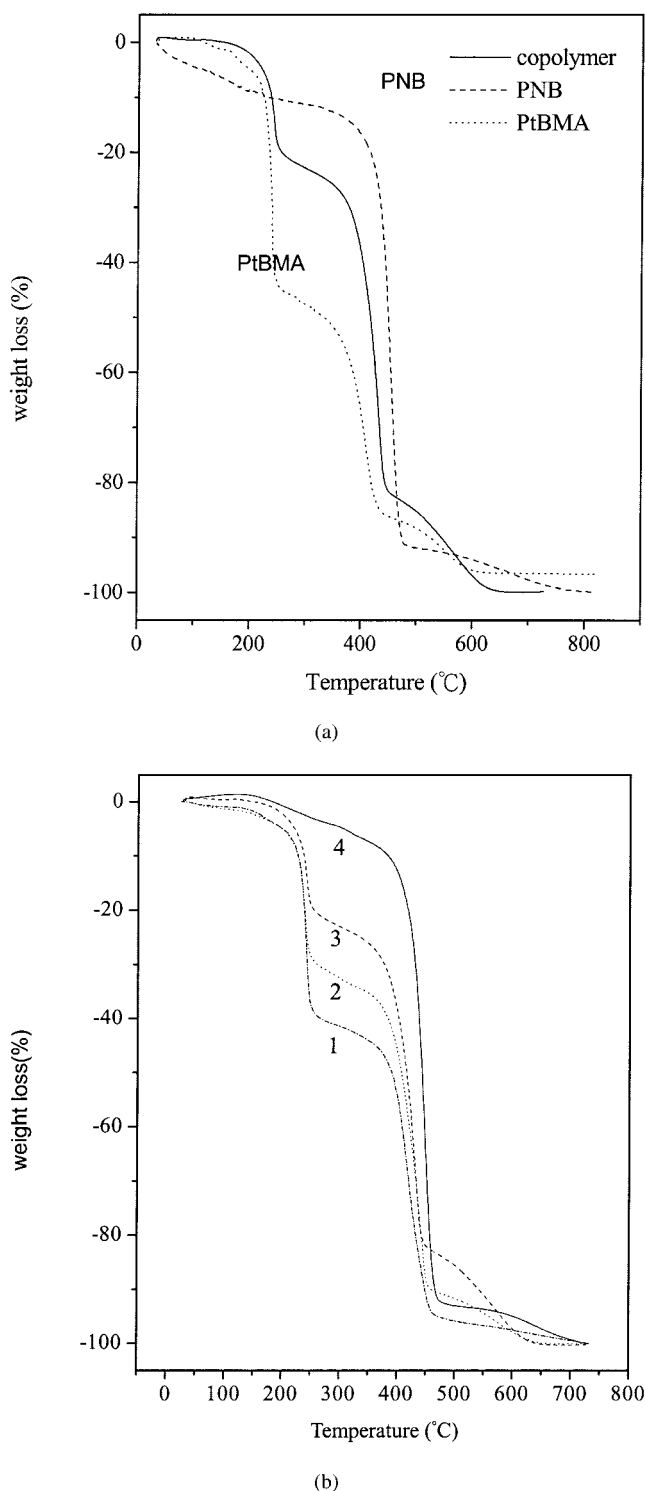


Figure 14 TGA thermograms for (a) the homopolymers and copolymer of NB and tBMA and (b) the copolymers of NB and tBMA with different NB/tBMA feed compositions: (1) 12/88, (2) 22/78, (3) 30/70, and (4) 87/13.

tive way according to the trigger mechanism proposed by Yestene.⁴⁰ This mechanism can properly explain the complex copolymerization behavior because the complexation of the first monomer is a step distinctly

different from the propagation step. Therefore, different monomers may have different abilities to activate the catalytic center to produce different numbers of active species. These active centers are never free in this mechanism; they are always accompanied by a complexed monomer. The complexed monomer will insert into the growing chain only if another monomer is ready to be complexed. On this basis, we assume that the propagation step may proceed via a trigger mechanism and that the complexed monomer is inserted only if a new monomer is available to be complexed. Considering the strain effect of the cycloring, we may assume that NB has a stronger tendency to complex with the cationic nickel center than tBMA. As a result, the NB monomer is readily available to trigger the insertion of previously complexed NB or tBMA into the growing polymer chain and complexes itself with the cationic center. A tBMA monomer is also able to trigger a complexed tBMA, but its ability to force the insertion of already complexed NB into the polymer chain and complex itself with the nickel center is rather weak. The latter trigger action is possible, but its probability is very low and increases slowly with an increase in the tBMA concentration.

Therefore, NB displays a much higher rate of incorporating into the polymer chain than tBMA in NB/tBMA copolymerization. The use of a higher concentration of tBMA may slightly increase the complexation and incorporation of tBMA, but the tBMA monomer is unable to trigger and replace the complexed NB monomer. As a result, the extent of tBMA incorporation into the polymer is significantly less (in agreement with the experimental reactivity ratio; see Fig. 10) and results in lower reactivity. However, the tBMA polymerization is strongly inhibited by the presence of a small amount of NB. As previously assumed, nickel centers will complex preferentially with NB, but the NB content is rather low. Polymerization must proceed by tBMA complexation, as mentioned previously. On the contrary, the ability of NB complexed with the nickel center is very slow. In agreement with our assumption based on the trigger mechanism involved in this polymerization system, Peruch et al.²³ and Zhao et al.²⁶ reported a similar case for the homopolymerization and copolymerization of NB and styrene in the presence of the nickel-based/MAO system. However, a detailed kinetic investigation of both the homopolymerization and copolymerization of NB and tBMA initiated by the $\text{Ni}(\text{acac})_2/\text{MAO}$ system is necessary to provide further evidence supporting our assumption.

CONCLUSIONS

The homopolymerization and copolymerization of tBMA and NB with $\text{Ni}(\text{acac})_2$ in combination with MAO were successfully performed. For these copoly-

merizations, a gradual loss in the reactivity was found with the addition of tBMA to NB or of NB to tBMA because of the trigger coordination mechanism. The determination of the reactivity ratios indicated a much higher reactivity for NB than for tBMA ($r_{\text{NB}} = 4.14$ and $r_{\text{tBMA}} = 0.097$); this was interpreted with the coordination mechanism.

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