

Synthesis and characterization of poly(norbornene) substituted with phthalimide and ammonium groups via living ring-opening metathesis polymerization

Der-Jang Liaw^{*}, Chih-Hung Tsai

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 106 Taiwan

Abstract

2-Norbornene-5-methylphthalimide (NBEPI) was prepared to synthesize an amino group containing poly(norbornene) via living ring-opening metathesis polymerization (ROMP) using a well-defined catalyst $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$. The resulting poly(NBEPI) was of high molecular weight and had a reasonably narrow molecular weight distribution ($\overline{M}_n = 298,900$ and $\text{PDI} = 1.22$). The glass transition temperature (T_g) of poly(NBEPI) is 140°C . The 10% decomposition temperature of poly(NBEPI) is 410°C . Hydrazinolysis of poly(NBEPI) gave poly(2-norbornene-5-methylamine), poly(NBEMA). Though insoluble in almost all organic solvents, poly(NBEMA) becomes soluble in water after quaternization of the amine groups by gaseous HCl. Because of the living nature of the polymerization of NBEPI, poly(NBEMA) is reasonably linear and has a well-controlled molecular weight. The hydrogenation of poly(NBEPI) by diimide generated in situ from *p*-toluenesulfonylhydrazide decreased the T_g but increased thermal stability. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Living ROMP; NBEPI; NBEMA; Glass transition temperature

1. Introduction

Living ring-opening metathesis polymerization (ROMP) is a well-controlled procedure, which in favorable circumstances can allow the construction of well-defined macromolecular structure with a high level of precision [1]. One of the main reasons for the limitation of the development of the olefin metathesis reaction in polymer synthesis is the high reactivity of most catalyst with functional groups bearing heteroatoms [2].

Maughon and Grubbs have shown well-controlled living polymerization of cyclobutene substituted with secondary amine with well-defined Ru complex $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ [3], but norbornene (NBE) substituted with primary amine has not been investigated with the above Ru complex. Larroche et al. [2] reported that norbornene derivatives having amino and ammonium groups could be polymerized by the catalyst $\text{W}(\text{CO})_3(\text{arene})$ associated with large excess of organoaluminum com-

^{*} Corresponding author. Tel.: 886-2-27335050, 886-2-27376638; Fax.: 886-2-27376644, 886-2-23781441; E-mail: liaw@ch.ntust.edu.tw

pounds and molecular oxygen. However, the solubility is almost zero for amino-containing polymers [2]. Most catalyst systems which are active in norbornene metathesis were found to be inactive when norbornene was substituted with amine groups [2]. It is interesting to examine whether norbornene derivatives having functional amino group (such as 2-norbornene-5-methylamine, NBEMA) can be polymerized by $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$; and whether linear, low polydispersity poly(NBEMA) can be obtained by the above-mentioned Ru complex.

It is well-known that the phthalimide is one of the most useful protective groups for synthesizing primary amine substituent. In this study, 2-norbornene-5-methylphthalimide (NBEPi) was synthesized in which phthalimide was used as a protective group. In principle, linear and low polydispersity poly(NBEPi) can be used as the precursor to linear poly(NBEMA) with a narrow molecular weight distribution.

In addition, poly(NBEMA) can be quaternized by gaseous HCl to obtain water-soluble polymers. The nature of living polymerization of NBEPi will be investigated in detail. The thermal properties of poly(NBEPi) and hydrogenated poly(NBEPi) will also be discussed.

2. Experimental

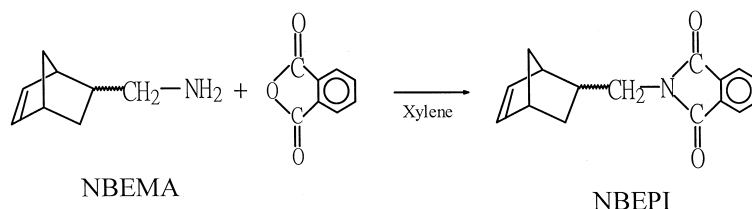
2.1. Materials

All chemicals were used as received without purification unless otherwise noted. Bis(tricyclohexylphosphine)-benzylideneruthenium dichloride $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ was purchased from Strem, USA. Dicyclopentadiene and allyl amine were purchased from Merck, Germany. Phthalic anhydride, hydrazine monohydrate, *p*-toluenesulfonylhydrazide and 2,6-di-*tert*-butyl-4-methyl-phenol were purchased from Acros, Belgium. Solvents such as xylene and ethanol were purified by normal procedures and handled under moisture-free atmosphere. The polymerization solvent, dichloromethane, was dried over calcium hydride, and distilled before use. The synthesis of 2-norbornene-5-methylamine (NBEMA) is accomplished via the Diels–Alder condensation of freshly cracked cyclopentadiene and allyl amine (bp = 60–61°C/11 mm Hg), (lit. bp = 61 ~ 62°C/12 mm Hg) [4].

2.2. Monomer synthesis

2.2.1. 2-Norbornene-5-methylphthalimide (NBEPi)

Since ring-opening metathesis polymerization of NBEMA having functional amino group could not be successfully carried out by $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$, 2-norbornene-5-methylphthalimide (NBEPi) was synthesized in which phthalic anhydride was used as a protective agent [5]. NBEPi was prepared by azeotropic removal of water from an equimolar solution of NBEMA and phthalic anhydride in xylene. After removing the solvent, the residue was recrystallized from *n*-hexane, m.p. = 99–100°C. The reaction is shown below.



[endo/exo = 85:15, ^1H NMR (400 MHz, CDCl_3), Fig. 1a, 6.15 (m, =CH, endo), 6.06 (m, =CH, endo), 5.95 (m, =CH, exo), 7.75, 7.60 (m, 4H, aromatic)]. ^{13}C NMR (100 MHz, CDCl_3) δ /ppm: 168.1, 137.3, 136.6, 135.8, 133.5, 132.4, 131.8, 122.8, 49.3, 44.9, 44.3, 44.2, 43.0, 42.4, 41.8, 41.7, 38.1, 38.0, 30.6. IR (KBr pellet, cm^{-1}); 1618($\nu_{\text{C}=\text{C}}$, vinylic), 1700($\nu_{\text{C}=\text{O}}$, symmetric), 1758($\nu_{\text{C}=\text{O}}$, asymmetric). UV(THF): λ_{max} : 218.4 nm, $\epsilon = 4.21 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.

2.3. Polymerization

A typical polymerization is as follows (Scheme 1). A solution of catalyst was prepared by dissolving $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ (2 mg, 2.45×10^{-3} mmol) in 1 ml of anhydrous methylene chloride under argon-filled dry-box. The monomer 2-norbornene-5-methylphthalimide (NBEPi) (0.62 g, 2.45 mmol) was dissolved in 5 ml of methylene chloride and then degassed via a freeze–pump–thaw cycle. After it was degassed completely, the catalyst solution was injected into the monomer solution by syringe. The solution was vigorously stirred at room temperature for 2 h. The color of the solution changed from pink to yellow after the reaction was carried out at 25°C for 10 min. The polymerization was terminated by the addition of a small amount of ethyl vinyl ether. After termination, the

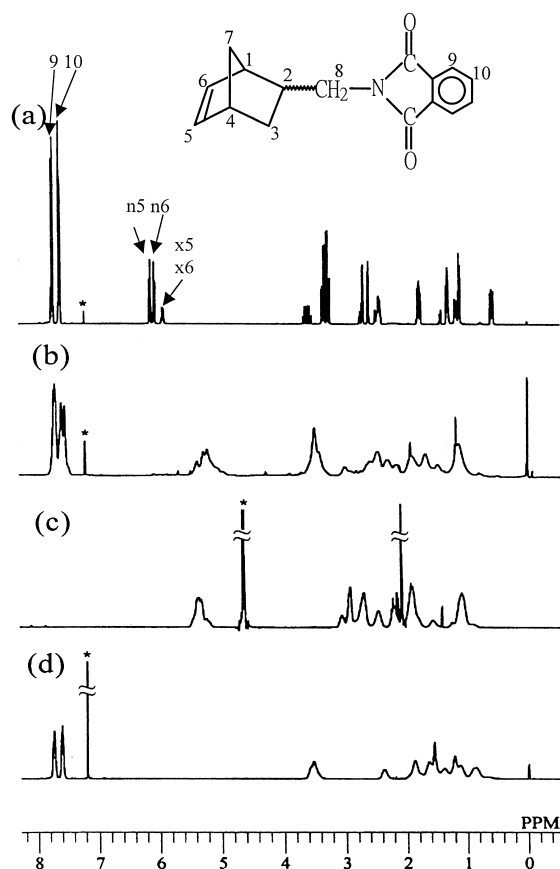
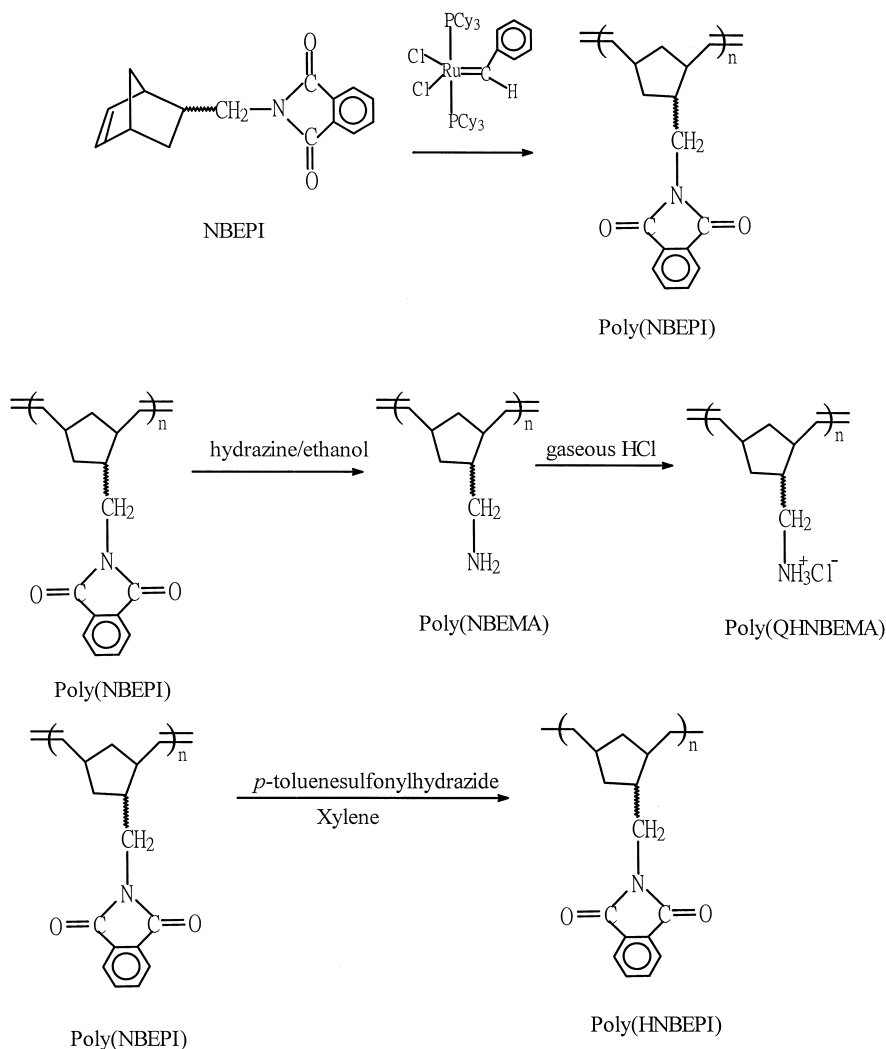


Fig. 1. 400 MHz ^1H NMR spectra (a) NBEPi (CDCl_3); n = endo, x = exo; (b) poly(NBEPi) (CDCl_3); (c) quaternized poly(NBEMA) with gaseous HCl, (D_2O); (d) hydrogenated poly(NBEPi), (CDCl_3). Starred peaks are due to solvent.



Scheme 1.

solution was stirred for an additional 5 min, and the polymer was precipitated in excess of methanol (250 ml) and dried overnight in a vacuum system at room temperature to give a flaky white solid in essentially quantitative yield. The resulting polymer was soluble in methylene chloride, chloroform and tetrahydrofuran (THF), but insoluble in dimethylsulfoxide (DMSO), and dimethylformamide (DMF). [^1H NMR (400 MHz, CDCl_3), Fig. 1b, 7.4–7.8 ppm (4H, aromatic), 4.5–4.6 ppm (2H, olefinic)], (GPC, Table 1, $[\text{M}]/[\text{I}] = 1000$, $\overline{M}_n = 298,900$ and $\text{PDI} = 1.22$).

2.4. Hydrazinolysis and quaternization of polymer

As in a typical experiment, [6] 0.2 g of poly(NBEPI) was suspended in 20 ml of ethanol in a Schlenk tube. To the above mixture were added hydrazine hydrate 2 ml and a trace of 2,6-di-*tert*-butyl-4-methyl-phenol. The mixture was degassed thrice via a freeze-pump-thaw cycle, then the tube

Table 1

Polymerization results for NBEPI in various [M]/[I] molar ratios by $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ at 25°C^{a,b}

[M]/[I] molar ratio	\overline{M}_n (calculated)	\overline{M}_n (observed)	PDI	T_g^c (°C)	$T_{d,10\%}^d$ (°C)
100	25,300	32,900	1.21	140	412
200	50,600	58,400	1.19	139	411
400	101,300	118,400	1.21	141	410
700	177,300	190,100	1.29	144	412
1000	253,300	298,900	1.22	142	400

^a[M] = 0.122 M, polymerization solvent: methylene chloride.^bDetermined by GPC using polystyrene calibration standards.^cAnalysis by differential scanning calorimetry with a scan rate of 10°C/min.^dAnalysis by thermal gravimetric analysis with a scan rate of 10°C/min.

was heated to 100°C. The polymer has become cotton-like and the mixture was gradually changed to a light yellowish homogeneous solution after 1 h. Hydrazinolysis was continued for 5 h and then the solution was cooled to room temperature. The quaternization of poly(NBEMA) was continuously carried out from the reaction of poly(NBEMA) with gaseous hydrochloride at room temperature for 2 h. The quaternized polymer was precipitated during the reaction period, and was dissolved in water, filtered and then precipitated from acetone. The polymer was collected and dried on a vacuum system at room temperature. [¹H NMR (400 MHz, CDCl₃), Fig. 1c, 2.0–2.2 ppm (3H, NH₃⁺), 5.2–5.6 ppm (2H, olefin)].

2.5. Hydrogenation of poly(NBEPI) [7]

As in a typical experiment, 0.2 g of poly(NBEPI) was dissolved in 20 ml of xylene in an ampoule. To the above solution were added 1.1 g (7.5 equiv. relative to the repeating unit) of *p*-toluenesulfonylhydrazide as a hydrogenation agent and a trace of 2,6-di-*tert*-butyl-4-methylphenol. The ampoule containing the polymer, solvent and hydrogenation agent was then degassed thrice via a freeze-pump-thaw cycle and sealed. Then, it was gradually heated to 120°C. At 100°C, a homogeneous solution resulted and nitrogen started to evolve. The solution was stirred at 120°C for 3 h until the evolution of nitrogen stopped. The solution was cooled to room temperature and precipitated with methanol. It was dissolved in methylene chloride and reprecipitated with methanol to further purify the white polymer. The polymer was dried in vacuum overnight at room temperature. Yield = 0.18 g. [¹H NMR (400 MHz, CDCl₃), Fig. 1d, the peak at 5.0–5.6 ppm (olefin) disappeared].

2.6. Characterization methods

Infrared spectra were measured in the range of 4000–400 cm⁻¹ for the polymer in KBr disks using JASCO IR-700 Spectrometer. Thermogravimetric analysis was measured on Du Pont 2200 instrument at a heating rate of 10°C min⁻¹ in nitrogen. The glass transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate of 10°C min⁻¹. Weight-average (\overline{M}_w) and number-average (\overline{M}_n) molecular weight were determined by gel permeation chromatography (GPC). Three Waters (Ultrastragel) columns 300 × 7.7 mm (500, 10³, 10⁴ Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 ml min⁻¹) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. ¹H NMR

and ^{13}C NMR spectra were taken on a JEOL EX-400 operating at 399.65 MHz for proton and 100.40 MHz for carbon.

3. Results and discussion

3.1. Polymerization and characterization

Since the ring-opening metathesis polymerization of NBEMA having amino group did not occur, NBEPI was synthesized using $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ as shown in Scheme 1. The polymerization of NBEPI was observed to proceed smoothly in methylene chloride at room temperature, affording homopolymer in high yield (more than 98%). For comparison, ^1H NMR spectra of both the monomer and polymer are shown in Fig. 1a and b, respectively. Integration of the aromatic (7.4–7.8 ppm) and olefin regions (4.8–5.6 ppm) (Fig. 1b) of the spectrum gives the expected 2:1 ratio, providing further confirmation of the polymer structure [8].

In order to fully investigate the polymerization, the dependence of the number average molecular weight (\overline{M}_n) on the $[\text{M}]:[\text{I}]$ ratio was studied ($[\text{M}]$ = monomer concentration, $[\text{I}]$ = initiator concentration). The dependence was linear for polymerization of NBEPI providing control over the polymer molecular weight, and the polymers produced were of low polydispersity between 1.2 and 1.3 for all ratios (Table 1 and Fig. 2). The linear dependence observed was supportive of a living polymerization [3], but further proof was necessary. In addition to the molecular weight study, evidence for the lack of chain transfer and chain termination reaction must be demonstrated to prove that a polymerization is in progress. A sequential monomer addition experiment was run for NBEPI. Using complex $1\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$, 100 equiv. of NBEPI were polymerized for 1 h under typical condition. The solution was then divided into three portions. Portion A was removed and its molecular weight was determined by GPC. Portion B was stirred for an additional 5 h. An additional 200 equiv. of NBEPI, was added to portion C and stirred for another 1 h before being terminated. Portions B and C were then analyzed by GPC.

As seen in Fig. 3, no significant change was observed from the 1 h reaction (A) or 6 h reaction (B). If any significant chain transfer processes had been operative during this time, broadening of the PDI

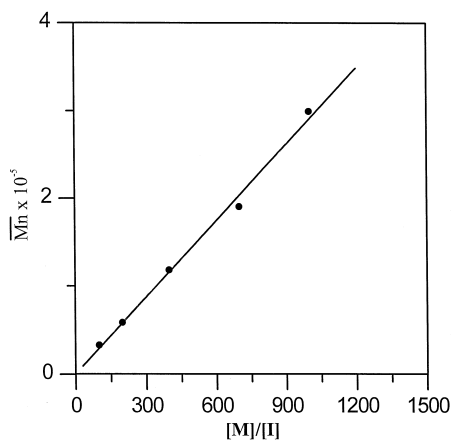


Fig. 2. Molecular weight dependence of the polymerization of NBEPI on $[\text{M}]/[\text{I}]$.

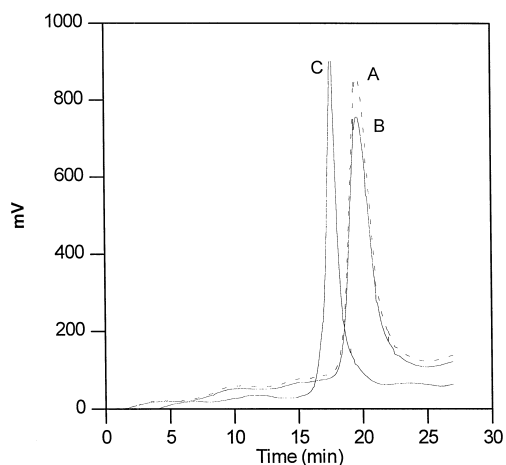


Fig. 3. Sequential monomer addition experiment (A) with 100 equiv. of NBEPI after 1 h, (B) with 100 equiv. of NBEPI after 6 h and (C) after an additional 200 equiv. of NBEPI was added.

$(\overline{M}_w/\overline{M}_n)$ would have been observed. Portion C in which an additional 200 equiv. of NBEPI had been polymerized resulting in an $\overline{M}_n = 96,400$ and $PDI = 1.28$. A clean shift in the GPC peaks was accomplished, proving that no chain termination processes had occurred. Chain termination would have resulted in inactive chain ends after polymerization of the first 100 equiv. of NBEPI which would produce a bimodal GPC trace after additional polymerization. The absence of both chain transfer and chain termination reaction was indicative of a living polymerization of NBEPI [3].

3.2. Hydrazinolysis of poly(NBEPI), [poly(NBEMA)] and quaternization of poly(NBEMA), [poly(QHNBEMA)]

The hydrazinolysis of poly(NBEMA) was carried out by using hydrazine-hydrate to obtain amino-containing poly(norbornene) as shown in Scheme 1. The solution was poured into acetone to precipitate poly(NBEMA). The IR spectrum (KBr disc) of poly(NBEMA) showed new absorption at 3380 cm^{-1} (amino group), and the imide absorptions at 1762 and 1705 cm^{-1} had completely disappeared. The poly(NBEMA) obtained was almost insoluble in almost all organic solvents. However, it can become soluble in water by quaternization of the amino group with gaseous HCl. The ^1H NMR for quaternized poly(NBEMA), [poly(QHNBEMA)], is shown in Fig. 1c (supra); with the peak of NH_3^+ between 2.0 and 2.2 ppm. Integration of the NH_3^+ (2.0–2.2 ppm) and olefin regions (5.2–5.6 ppm) of the spectrum gives the expected 3:2 ratio, providing further confirmation of the quaternized poly(NBEMA) structure. Because of the living nature of the polymerization of NBEPI, poly(NBEMA) and poly(QHNBEMA) are reasonably linear and have a well-controlled molecular weight.

3.3. Hydrogenated poly(NBEPI), [poly(HNBEPI)]

Since thermal instability of poly(NBEPI) is largely due to unsaturation of the main chain, poly(NBEPI) was hydrogenated by *p*-toluenesulfonylhydrazide. In a previous study [9], diimide ($\text{NH}=\text{NH}$) has been used for the hydrogenation of olefinic compounds and unsaturated polymer. An important feature of diimide hydrogenation is its selectivity. Only non-polar double bonds are active;

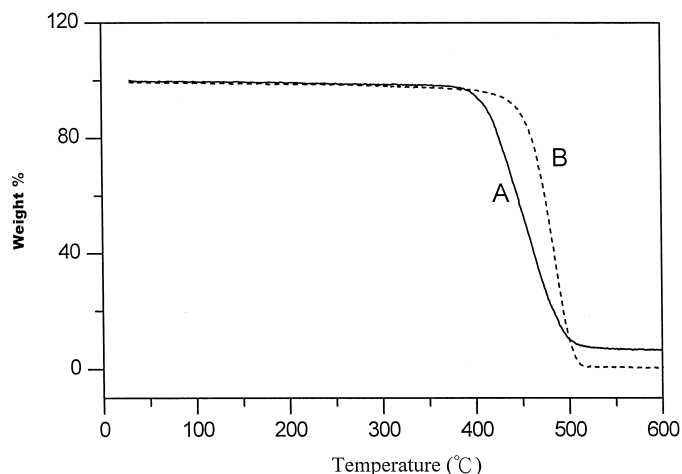


Fig. 4. TGA curves for poly(NBEPI) (A) and hydrogenated poly(NBEPI) (B) measured under nitrogen. Temperature was raised at rate of 10°C/min.

polar double bonds and aromatic ring systems are inert. The *p*-toluenesulfonylhydrazide was used as a convenient precursor to diimide generation in situ [10]. The ^1H NMR spectrum of the poly(HNBPI) was obtained in deuterated chloroform (Fig. 1d). There was no olefinic resonance visible after hydrogenation. That is, before hydrogenation (Fig. 1b), there were olefinic resonances between 5.0 and 5.6 ppm; and after hydrogenation (Fig. 1d), the resonances completely disappeared. The aromatic resonances of poly(HNBPI) between 7.4 and 7.8 ppm, (Fig. 1d) still existed, suggesting that the phthalimide group remained unchanged. The solubility of poly(HNBPI) is almost the same as poly(NBEPI).

3.4. Thermal properties of poly(NBEPI) and poly(HNBPI)

Analysis of the thermal properties of various poly(NBEPI)s having different molecular weights was undertaken using both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 1, *supra*). The T_g values for these polymers ranged from 139–144°C and no melting transitions were observed for any of the molecular weight of poly(NBEPI). TGA results were compared using the $T_{d,10\%}$, the temperature at 10% decomposition. $T_{d,10\%}$ values between 400 and 410°C were observed in nitrogen atmosphere and no remarkable difference was found. Since $T_{d,10\%}$ is more than 410°C, poly(NBEPI)s having phthalimide group could be considered as a thermally stable material. Saturation of the double bond for poly(NBEPI) leads to an increase of about 35°C in decomposition temperature under nitrogen (Fig. 4); while a decrease in T_g of the hydrogenated polymer was about 20°C. Obviously, the rotation around the hydrogenated carbon–carbon single bond made the mobility of the polymer chain easier [11].

4. Conclusions

The polymerization of NBEPI with $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ possessed low dispersity and well-controlled molecular weight. The hydrazinolysis of poly(NBEPI) by hydrazine resulted in the amino substituted poly(norbornene), poly(NBEMA), which is insoluble in almost all organic solvents.

However, poly(NBEMA) quaternized by HCl becomes soluble in water. Because of the living nature of the polymerization of NBEPI, the poly(NBEMA) is reasonably linear and has a well-controlled molecular weight. Hydrogenated poly(NBEPI) had an increase of about 35°C in decomposition temperature under nitrogen, but an decrease in T_g of about 20°C compared with poly(NBEPI). All polymer structures could be successfully explained by ^1H NMR spectra.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for their financial support.

References

- [1] P. Dounis, W.J. Feast, *Polymer* 37 (1996) 2547.
- [2] J. Larroche, J.P. Laval, A. Lattes, J.M. Basset, *J. Org. Chem.* 49 (1984) 1886.
- [3] B.R. Maughon, R.H. Grubbs, *Macromolecules* 30 (1997) 3459.
- [4] W.E. Bachmann, L.F. Fieser, A.H. Blatt, J.R. Johnson, *Organic Reaction*, Vol. 4, Roger Adams, New York, 1948, pp. 60–173.
- [5] T.W. Greene, *Protective Groups in Organic Synthesis*, Wiley, New York, 1980, p. 265.
- [6] A.R. Mitchell, S.B.H. Kent, M. Engelhard, R.B. Merrifield, *J. Org. Chem.* 43 (1978) 2845.
- [7] Z. Wu, R.H. Grubbs, *Macromolecules* 27 (1994) 6700.
- [8] J. Gratt, R.E. Cohen, *Macromolecules* 30 (1997) 3137.
- [9] C.E. Miller, *J. Chem. Ed.* 42 (1965) 254.
- [10] B.H. Shon, J.A. Gratt, J.K. Lee, R.E. Cohen, *J. Appl. Polym. Sci.* 58 (1995) 1041.
- [11] Y. Yoshida, K. Goto, Z.J. Komiya, *Appl. Polym. Sci.* 66 (1997) 367.