# Polynorbornene with Cross-Linkable Side Chains via Ring-Opening Metathesis Polymerization

**Der-Jang Liaw,* Jang-Shiang Tsai, and Pi-Ling Wu**

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

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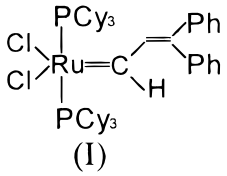
ABSTRACT: The ring-opening metathesis polymerization (ROMP) of 5-(methyl methacryloyl isocyanate)-bicyclo[2.2.1]hept-2-ene [i.e., norbornene containing methacryloyl isocyanate (NBMMAI)] having cyclic olefin and terminal double bond was investigated in order to produce novel polymers with cross-linkable side chains under ligand exchange with MMA by using $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ (**II**) as catalyst. Results of infrared spectra, $^1$H NMR, and $^{13}$C NMR showed that poly(NBMMAI) contains polynorbornene backbone ring structure and methacryloyl side chains. The $^1$H NMR spectrum of poly(NBMMAI) showed new vinyl protons as a broad signal between 5.15 and 5.37 ppm in the ratio of 0.4 and 2.8, corresponding to the vinyl protons of the cis and trans double bond of the ring-opened polymer, respectively. Gel formation was still observed in the polymerization of NBMMAI using ruthenium catalyst **II** with 20 mol % *p*-methoxyphenol (MEHQ). An increase in bulkiness of the ligand reduced the cross metathesis reaction and led to reduced activity for the catalyst. Increasing the ratio of monomer concentration [M] to catalyst [cat] resulted in the formation of higher molecular weight polymers and polymer yield. The incorporation of poly(NBMMAI) into poly(methyl methacylate) (polyMMA) to produce AB cross-linked materials was accomplished. These cross-linked materials had higher thermal stability and solvent resistance than pure polyMMA.

## Introduction

Increasing interest in ring-opening metathesis polymerization (ROMP) of norbornene derivatives containing functional groups has developed over recent years with the aim of obtaining polymer structures with attractive properties.[1] Cross-linkable polymers have found a wide demand in the domain of interpenetrating polymer networks,[2] nonlinear optical materials,[3] macro- and microlithography,[4] and the formation of more thermally and chemically resistant materials.[5]

One of the most widely employed cross-linkable side chains is the methacryloyl group, which polymerizes both thermally and photochemically in the presence of free-radical initiators and photosensitizers, respectively. Because of the sensitivity of many metathesis catalysts to functional groups, the use of ROMP in the formation of these cross-linkable polymers has been limited.

Grubbs et al. reported the polymerization of 5-methacryloyl-1-cyclooctene having cross-linked side chain with ruthenium catalyst **I**.[6]

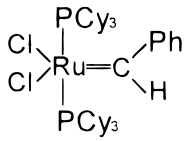



(I)

Cy=cyclohexyl

Ph=phenyl

Gel formation was observed when catalyst **I** was used without *p*-methoxyphenol (MEHQ) during polymerization. The results supported the free-radical mechanism of cross-linking.[6] Moreover, Grubbs et al. also reported that a well-defined ruthenium catalyst **II** has allowed the ROMP of a series of functionalized cyclooctenes.[7,8] The high functional group tolerance of the catalyst has prompted an investigation of the use of ROMP in the formation of cross-linked polymers.




(II)

Cy=cyclohexyl

Ph=phenyl

In this study, a new functional monomer 5-(methylmethacryloyl isocyanate)bicyclo[2.2.1]hept-2-ene [i.e., norbornene containing methacryloyl isocyanate (NBMMAI)] was synthesized by the reaction of 5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene ($NBCH_2OH$) and methacryloyl isocyanate (MAI). It is interesting to investigate the reactivity of ROMP of NBMMAI having methacryloyl and cyclic norbornene groups by using ruthenium catalyst **II** as an initiator. The structure of poly(NBMMAI) was identified by IR, $^1$H NMR, and $^{13}$C NMR. The effects of various ligands and monomer/catalyst ratios on polymer yield, molecular weight, and molecular weight distribution were also investigated. Reaction of this multifunctionalized methacryloyl polymer with methyl methacrylate under free-radical polymerization conditions has led to the formation of AB cross-linked system of poly(methyl methacrylate) (polyMMA). The thermal properties of AB cross-linked polyMMA were measured.

## Experimental Section

**Materials.** 5-(Hydroxymethyl)bicyclo[2.2.1]hept-2-ene ($NBCH_2OH$) was prepared as reported by Bachmann et al.:[9] bp 92−95 °C/13 mmHg; yield = 40%; exo/endo = 20/80. Bis-

* To whom correspondence should be addressed. Phone 886-2-27376638, 886-2-27335050; FAX 886-2-23781441 or 886-2-27376644; E-mail liaw@ch.ntust.edu.tw.

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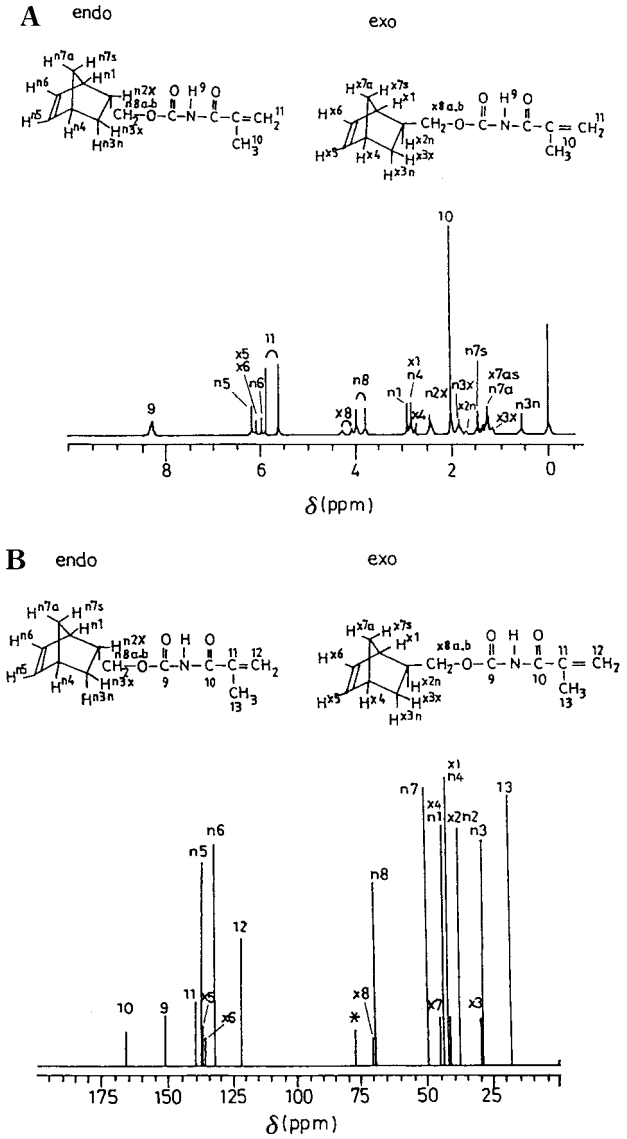



**Figure 1.** NMR spectra of NBMMAI monomer taken in $CDCl_3$: (A) $^1H$ NMR and (B) $^{13}C$ NMR. Starred peak is due to the presence fraction of solvent ($CDCl_3$).

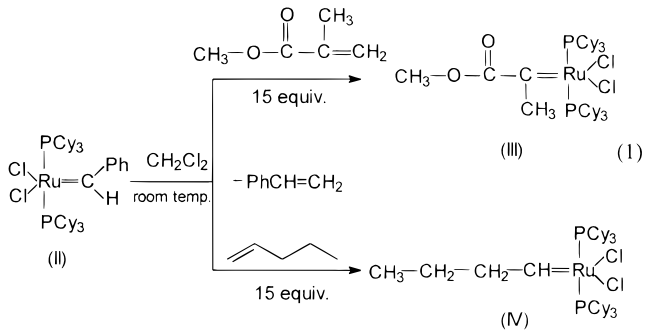
(tricyclohexylphosphine)benzylideneruthenium dichloride was purchased from Strem. Dicyclopentadiene and allyl alcohol were purchased from Merck. Methacryloyl isocyanate was supplied by Nippon Paint Co. *p*-Methoxyphenol, methyl methacrylate (MMA), 1-pentene, and 3,3-dimethyl-1-butene were purchased from Aldrich and used without further purification. Solvents were purified by normal procedures and handled under moisture-free atmosphere.

**Monomer Preparation.** 5-(Hydroxymethyl)bicyclo[2.2.1]-hept-2-ene (20 g, 0.160 mol) and methacryloyl isocyanate (MAI) (19.5 g, 0.175 mol, 10% excess) were added to ethyl acetate and kept at room temperature for 4 h. The product thus obtained was a white solid (mp = 93−95 °C). The yield is 80% and exo/endo = 20/80. The NMR spectra of the monomer are shown in Figure 1. The spectra agree satisfactorily with the proposed structure.

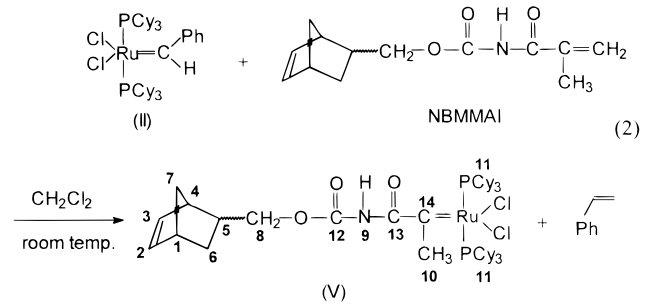
**Ligand Exchange of Catalyst II with MMA or with 1-Pentene.**[10] Catalyst **II** (823 mg, 1.0 mmol) and MMA (15 equiv) were dissolved in 10 mL of methylene chloride. After a freeze−pump−thaw cycle, the solution was stirred at room temperature for 30 min. The solvent and the residue were removed under vacuum. The product **III** was dried under vacuum for several hours. $^1H$ NMR ($CDCl_3$): $\delta$ 2.45 (Ru=CC$H_3$), 4.08 (COOC$H_3$), 2.29, 1.91−1.77, 1.67, 1.34, 1.19 [P($C_6H_{11}$)$_3$]. $^{13}C$ NMR ($CDCl_3$): $\delta$ 295.73 (Ru=*C*CH$_3$), 169.08 (*C*OOCH$_3$), 51.48 (COOC$H_3$), 31.31, 29.06, 28.72, 25.60 [P($C_6H_{11}$)$_3$], 17.54 (Ru=C*C*H$_3$).

The complex **IV** having 1-pentene moiety was prepared in analogy to **III**, using catalyst **II** and 1-pentene as starting materials. $^1H$ NMR ($CDCl_3$): $\delta$ 18.86 (Ru=C*H*), 2.69 (Ru=CHC$H_2$), 2.42, 1.88−1.83, 1.74−1.65, 1.48−1.37, 1.27−1.18, 0.83 [C$H_2$C$H_3$ and P($C_6H_{11}$)$_3$]. $^{13}C$ NMR ($CDCl_3$): $\delta$ 305.99 (Ru=*C*H), 57.69 (*C*HCH$_2$), 34.27, 30.14, 27.76, 26.91 [P(*C*$_6$H$_{11}$)$_3$], 21.88 (*C*H$_2$CH$_3$), 12.79 (CH$_2$*C*H$_3$).

The reaction scheme is as follows:




**Equimolar Reaction between Catalyst II and NBMMAI.** Catalyst **II** (82.3 mg, 0.1 mmol) and NBMMAI (23.5 mg, 0.1 mmol) were dissolved in 10 mL of methylene chloride. After a freeze−pump−thaw cycle, the solution was stirred at room temperature for 30 min. The solvent and the residue were removed under vacuum. The product **V** was dried under vacuum for several hours. $^1H$ NMR ($CDCl_3$): $\delta$ 8.36 ($H_9$), 5.75−5.24 ($H_2$, $H_3$), 4.07 ($H_8$), 3.08 ($H_1$, $H_4$), 2.44 ($H_{10}$), 1.90−0.8 ($H_5$, $H_6$, $H_7$, $H_{11}$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 303.2 ($C_{14}$), 166.23 ($C_{13}$), 151.11($C_{12}$), 139.59, 134.64, 132.90, 130.44 ($C_2$, $C_3$), 67.66 ($C_8$), 51.02 ($C_7$), 43.77 ($C_4$), 41.96 ($C_1$), 35.59 ($C_5$), 34.78, 29.93, 27.06, 26.89 ($C_{11}$), 26.03 ($C_6$), 18.34 ($C_{10}$).




**Polymerization.** *Polymerization of NBMMAI Using Catalyst **II**.* The monomer NBMMAI (588 mg, 2.5 mmol) was dissolved in 4 mL of methylene chloride. After a freeze−pump−thaw cycle, the solution of catalyst **II** (2 mg, $2.5 \times 10^{-3}$ mmol) in 1 mL of methylene chloride was injected to the monomer solution. Then the solution was stirred at room temperature. The slight purple color changed rapidly to light yellow. The solution became gel-like after 10 min, and the resulting polymer was not soluble in common organic solvents.

*Polymerization of NBMMAI Using the Complex Having MMA Moiety.* A solution of the complex having MMA moiety was prepared by dissolving catalyst **II** (2 mg, $2.5 \times 10^{-3}$ mmol) in 4 mL of methylene chloride and 0.5 mL of MMA. After a freeze−pump−thaw cycle, the slight purple color changed to light brown when the ligand exchange was accomplished.

The monomer NBMMAI (588 mg, 2.5 mmol) was dissolved in 4 mL of methylene chloride and added to the tube using a syringe. Polymerization was carried out at 30 °C for 2 h. The viscous reaction solution was terminated by the addition of trace ethyl vinyl ether (0.1 mL). The solution was continuously stirred for another 10 min, and then polymer was precipitated in excess methanol. $^1H$ NMR (DMSO-$d_6$): $\delta$ 10.38 (s, 1H), 5.79−5.56 (bm, 2H), 5.37−5.15 (bm, 2H), 4.02−3.81 (bm, 2H), 3.70−3.14 (bm, 2H), 1.82−1.66 (bm, 5H), 1.19 (s, 3H) (Figure 2). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 166.46, 151.24, 138.62, 134.17,

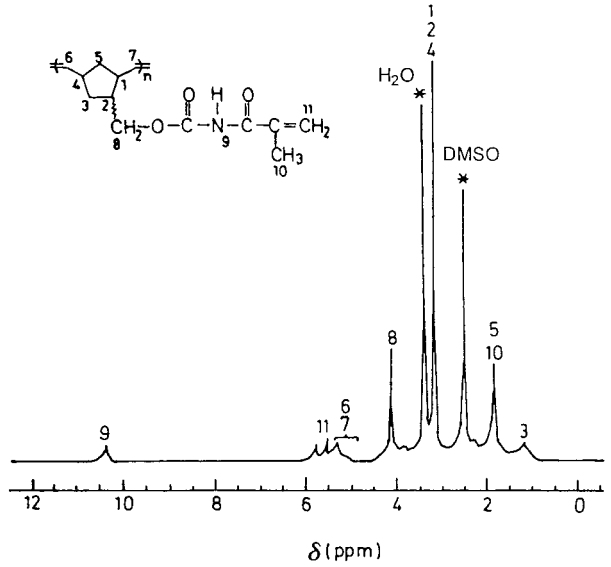



**Figure 2.** $^1$H NMR spectrum of poly(NBMMAI) taken in DMSO-$d_6$. Starred peak is due to the presence fraction of solvent.

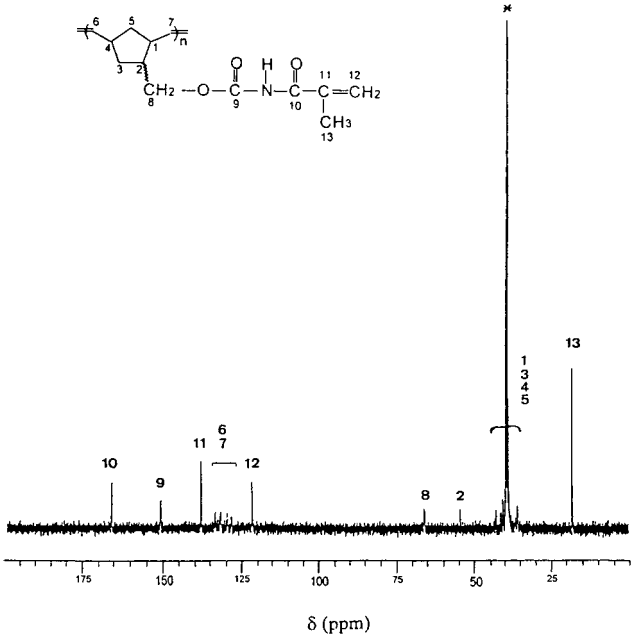


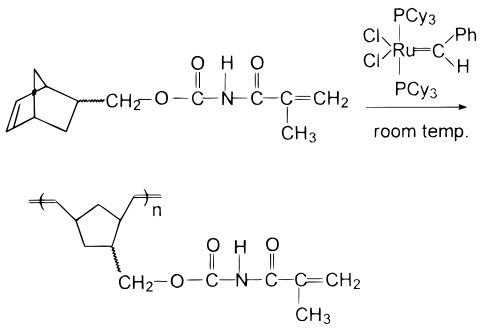

**Figure 3.** $^{13}$C NMR spectrum of poly(NBMMAI) taken in DMSO-$d_6$. Starred peak is due to the presence fraction of solvent.

132.49, 130.31, 128.96, 122.43, 66.47, 54.85, 43.20, 41.55, 39.09, 36.07, 18.31 (Figure 3). IR (neat): 3270, 2936, 2850, 1749, 1695, 1625, 1502, 1390, 1283, 1209, 1165, 1031, 998, 965, 938, 660.

**Instruments.** Infrared spectra were measured in the range 4000−400 cm$^{-1}$ for the polymer in KBr disks using a JASCO IR-700 spectrometer. Thermogravimetric analysis was measured on Du Pont 2200 instrument at a heating rate of 10 °C/min in nitrogen. $^1$H 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. The inherent viscosity for polymer was measured at 0.5 g/dL in DMAc using an Ubbelohde viscometer operating at 30 °C. Weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weight were determined by gel permeation chromatography (GPC) at room temperature. Polystyrene was used as the standard. Four Waters (Ultrastyragel) columns 300 × 7.7 mm (500, 10$^3$, 10$^4$, and 10$^5$ 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.

## Results and Discussion

**Initial Polymerization Studies.** Initial polymerization was carried out as shown in the following scheme:




(3)

However, gel formation was observed during the polymerization without ligand exchange when benzene, toluene, or methylene chloride was used as solvent. The phenomenon was also observed by Grubbs et al.[6] in the polymerization of 5-methacryloyl-1-cyclooctene (MCO). However, they reported that the poly(MCO) with monomodal molecular weight distributions were formed in moderate yields without gel formation when 18 mol % *p*-methoxyphenol MEHQ was used. The polymer poly(NBMMAI) isolated from this gel was insoluble in all common organic solvents and was presumed to be highly cross-linked. There are two plausible explanations for the observed gelation. The first was free radical cross-linking of the side chain.[6] The second possible mechanism of cross-linking was cross metathesis reaction between methacryloyl groups and double bond of polymer chain.

To establish the free radical nature of the cross-linking process, the polymerization was studied in the presence of a free radical inhibitor. When 20 mol % MEHQ was used, gel formation was still observed for 10 min at room temperature. This phenomenon is quite different from the results of ROMP of 5-methacryloyl-1-cyclooctene.[6] The cross-linking mechanism for the polymerization of NBMMAI by catalyst **II** may be not only free radical but also cross metathesis reaction. To establish the cross metathesis nature of the cross-linking process, the equimolar reaction between catalyst **II** and NBMMAI was studied. From the $^1$H NMR spectrum, the peak at 19.91 ppm corresponding to Ru=CH of catalyst **II** disappeared; however, the peak at 2.44 ppm corresponding to Ru=C$CH_3$ of complex **V** appeared. From the results of NMR spectra, the structure of complex **V** could be identified; therefore, a possible reason for the cross-linking is the formation of the complex **V**.

**Influence of Various Ligands.** To reduce the reactivity of catalyst **II**, we used different alkene to exchange the ligand of ruthenium catalyst. Table 1 shows the results for the polymerization of NBMMAI by different ligands. According to Table 1, an increase in bulkiness of the ligand reduced the cross metathesis reaction leading to a decrease in the activity of the catalyst.[11,12] In general, ROMP with well-defined catalysts such as catalyst **II** proceeds on living manner.[13] So, the living propagating species in the case of the catalyst **II** and that of the complex derived from catalyst

**Table 1. Effect of Various Ligands on Yield and Molecular Weight for the Polymerization of NBMMAI Using Catalyst II[a]**

| polymer | ligand | polymer yield (%) | $\bar{M}_n$[b] | PDI[b] |
|---|---|---|---|---|
| 1 | styrene | gelation[c] | | |
| 2 | methyl methacrylate | 36 | 30 300 | 3.75 |
| 3 | 1-pentene | 23 | 16 100 | 3.14 |
| 4 | 3,3-dimethyl-1-butene | gelation[c] | | |

[a] Experimental conditions: monomer NBMMAI (2.5 mmol); catalyst **II** ($2.5 \times 10^{-3}$ mmol); [M]/[cat] = 1000; methylene chloride (4 mL); temperature 30 °C. [b] Molecular weight determined by GPC (polystyrene was used as a standard). [c] Gel formation during the polymerization.

**Table 2. Effect of [Monomer]/[Catalyst] Ratio on Polymer Yield, Molecular Weight, and Molecular Weight Distribution in the Polymerizaton of NBMMAI after Ligand Exchange with MMA[a,b]**

| polymer | [M]/[cat] | polymer yield (%) | $\bar{M}_n$[c] | PDI[c] |
|---|---|---|---|---|
| 5 | 1000 | 36 | 30 300 | 3.75 |
| 6 | 2000 | 78 | 68 800 | 1.38 |
| 7 | 4000 | 81 | 103 800 | 1.48 |
| 8 | 6000 | 82 | 185 700 | 1.62 |
| 9 | 8000 | 84 | 308 000 | 1.49 |

[a] Experimental conditions: catalyst **II** ($2.5 \times 10^{-3}$ mmol); methylene chloride (4 mL); temperature 30 °C. [b] Methyl methacrylate was used as ligand. [c] Molecular weight determined by GPC (polystyrene was used as a standard).

**II** and MMA are supposed to be the same. The major difference is initiation rate.[10]

From Table 1, poly(NBMMAI) could be obtained by using complex **III** and complex **IV**. However, gel formation was still observed after using the complex with catalyst **II** and 3,3-dimethyl-1-butene. It showed there was no reaction between catalyst **II** and 3,3-dimethyl-1-butene. This phenomenon was also reported by Grubbs et al.[10] The effect of the monomer to catalyst ([M]/[cat]) ratio after ligand exchange with MMA on polymer yield, molecular weight, and molecular weight distribution is shown in Table 2. The results showed that low [M]/[cat] ratios resulted in broad molecular weight distribution.[6] Increasing the [M]/[cat] ratio resulted in the formation of higher molecular weight polymers.[6,14] Also, this result might be caused by the presence of residual MMA. In ROMP, alkenes are known to act as transfer agent. Increase in molecular weight would be the result of increase of in [M]/alkene when [M]/[cat] was increased. The resulting polymer is soluble in dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and tetrahydrofuran (THF) but insoluble in chloroform. The polymer had inherent viscosity 1.71 dL/g (Table 2, polymer 5). The poly(NBMMAI) could be cast to obtain a transparent film.

**Characterization of Poly(NBMMAI).** The monomer (NBMMAI) and poly(NBMMAI) which was obtained after ligand exchange with MMA are characterized by IR spectra. The difference is that there is a strong band at 719 $cm^{-1}$ in the monomer and near 965 $cm^{-1}$ in the polymer, indicating that the ring-opened polynorbornene main chain has a predominant trans double bond.[15]

With respect to the $^1H$ NMR spectrum of poly(NBMMAI), as the vinylic proton peaks of norbornene ring at 5.88 and 6.01 ppm disappeared, the $^1H$ NMR of the polymer showed new vinyl protons as a broad signal between 5.15 and 5.37 ppm (Figure 2). These broad signals correspond to the vinylic protons of the cis and trans double bond of the ring-opened polymer, respectively. It allows us to estimate a cis and trans ratio of 0.14 for this polymer.[16] In the $^{13}C$ NMR spectroscope (Figure 3), the signal at 30−50 ppm is ascribed to the peaks of DMSO-$d_6$ and cyclic structure of the polymer. The various vinylic carbon peaks of the ring-opened polymer backbone appeared between 130 and 135 ppm. The signals at 121 and 138 ppm are due to the vinylene units of the methacryloyl group in the side chains. Considerable microstructural variety is possible in these systems, owing to the possibility of the head−tail additions and cis and trans vinylene units. Unfortunately, $^{13}C$ NMR was very complex with many overlapping multiplets or broad unresolved peaks, and it was impossible to interpret them in terms of microstructural detail, as is often possible for polymers produced by ROMP.[17,18]

**Synthesis of AB Cross-Linked Systems of Poly(NBMMAI) and PolyMMA.** The incorporation of the poly(NBMMAI) which was obtained after ligand exchange with MMA through chemical cross-links in polyMMA could be considered to improve thermal stability and chemical resistance of polyMMA. By polymerizing MMA in the presence of poly(NBMMAI), cross-links should form with the methacryloyl side chains of the poly(NBMMAI), thus yielding AB cross-linked material. Three different materials were made in this study. The monomer (NBMMAI) was dissolved in 4 mL of methylene chloride and added to the catalyst solution (catalyst **II** in methylene chloride) which was obtained after ligand exchange with MMA. After the polymerization (30 °C, 2 h), the solvent and MMA were completely removed by evaporator under reduced pressure, and a fixed amount of MMA was injected into the reactor to dissolve poly(NBMMAI). Benzoyl peroxide, 1% (w/w) based on MMA, was added to the polymer solution as a free radical initiatior. The weight ratios of poly(NBMMAI) to methyl methacrylate are 5, 10, and 15%. The solution of poly(NBMMAI) and MMA was degassed thrice via a freeze−pump−thaw cycle and then heated at 90 °C for 16 h. The MMA polymerized and cross-links were formed simultaneously with poly(NBMMAI). In accordance with the cross-linked derivative, the material was found to be insoluble in benzene, toluene, chloroform, and methylene chloride, but polyMMA was soluble in these organic solvents.

Further evidence for the cross-linking reaction was provided through thermal analysis using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). As shown in Figure 4A, the exothermal curve (>130 °C) indicates that the thermally initiated cross-linking reaction of the methacryloyl group occurred. However, in Figure 4B, upon cross-linking the system of poly(NBMMAI) and MMA, this curve disappeared, and no other distinctive phase transitions were observed. Since cross-linking generally enhances thermal stability, this should be reflected in the decomposition temperature ($T_d$), the temperature at which 10% weight loss occurs, as determined by TGA. As shown in Figure 5, the TGA results clearly demonstrated the difference in thermal stability among these materials. In the comparison of thermal stability among polyMMA, AB cross-linked materials, and pure poly(NBMMAI) (Figure 5E), the thermal stability of pure poly(NBMMAI) (Figure 5A) is higher than that of pure polyMMA and the interpenetrating (IPN) polymer of polyMMA

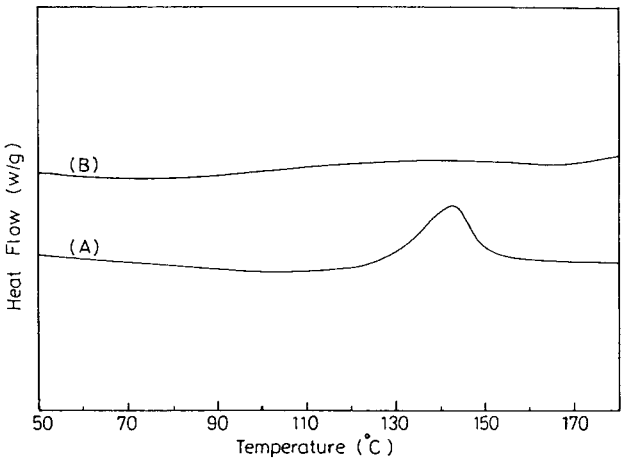



**Figure 4.** (A) Typical thermograms of poly(NBMMAI) and (B) its AB cross-linking material of poly(NBMMAI) and MMA. Data were obtained via DSC at a scan rate of 10 °C/min.

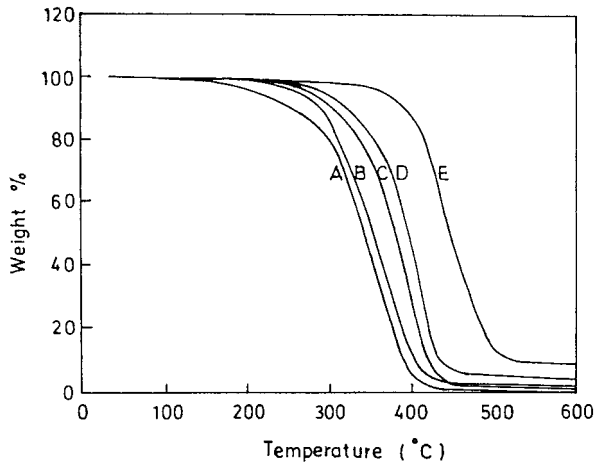



**Figure 5.** Comparison of thermal stability between polyMMA, AB cross-linked materials, and pure poly(NBMMAI): (A) 0% poly(NBMMAI); (B) 5% poly(NBMMAI); (C) 10% poly(NBMMAI); (D) 15% poly(NBMMAI); (E) 100% poly(NBMMAI) in a nitrogen atmosphere with a scan rate of 10 °C/min.

**Table 3. Comparison of Thermal Decomposition for the New Materials with PolyMMA**

| wt % of poly(NBMMAI) used in polymerization | $T_{d,10\%}$ (°C)[a] |
|---|---|
| 0% (100% polyMMA) | 250 |
| 5% (95% polyMMA) | 290 |
| 10% (90% polyMMA) | 305 |
| 15% (85% polyMMA) | 325 |
| 100% (0% polyMMA) | 405 |

[a] All values are obtained under an atmosphere of nitrogen at a scan rate of 10 °C/min.

and poly(NBMMAI) (Figure 5B−D). Increase in thermal stability of 40 °C [5% poly(NBMMAI)], 55 °C [10% poly(NBMMAI)], 75 °C [15% poly(NBMMAI)], and 155 °C [100% poly(NBMMAI)] was observed for the new materials relative to pure polyMMA (Table 3).

## Conclusions

An efficient synthesis of 5-(methyl methacryloyl isocyanate)bicyclo[2.2.1]hept-2-ene [i.e., norbornene containing methacryloyl isocyanate (NBMMAI)] was accomplished, and the ROMP of this monomer to create a cross-linked polymer using catalyst **II** after ligand exchange with MMA and 1-pentene was demonstrated. An increase in bulkiness of the ligands such as MMA and 1-pentene reduced the cross metathesis reaction and led to reduced activity of the catalyst. After ligand exchange with MMA, increasing the [M]/[cat] ratio resulted in the formation of higher molecular weight polymers. Poly(NBMMAI) has a predominant trans double bond in the main chain. The study of the AB cross-linked system of the poly(NBMMAI) with polyMMA gives rise to a new polyMMA material that had higher thermal stability than pure polyMMA.

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