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# Molecular architecture effect on reactivity of polynorbornenes with pendant α,β-unsaturated amide or ester bridged chains via ring-opening metathesis polymerization

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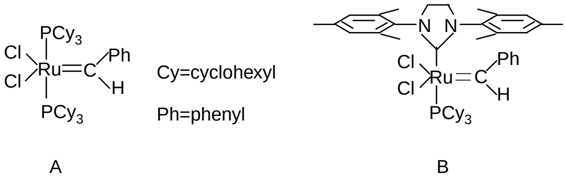
## Abstract

The molecular architecture effect on active structure of miscellaneous polynorbornenes (Scheme 1) was investigated with pendant α,β-unsaturated amide or ester groups via ring-opening metathesis polymerization (ROMP). Remarkable differences in the reactivity and polymerization behavior of active norbornenes depend on various molecular architectures. Polynorbornenes derived from active norbornenes with ethylene between urethane group and ester group such as **3a**,**b** (Scheme 1) showed excellent solubility. Organo-insoluble precipitate was obtained after ROMP of **5c** with the amide group. Random copolymerization technique of bicyclo[2.2.1]hept-2-ene (NB) and **5c** with amide group was considered to be a strategy to overcome the formation of precipitates, which expected to decrease the hydrogen bonding between two amide groups. High performance polynorbornenes with active groups could be designed with high potential of application for photoresist, UV curing and elastomers. Functional poly(**5b**) was incorporated into poly(methyl methacylate) [poly(MMA)] to produce AB cross-linked materials. The AB cross-linked material [15 wt% poly(**5b**), $T_{d10}=355$ °C in nitrogen] had higher thermal stability than pure poly(MMA) ($T_{d10}=250$ °C in nitrogen).

*Keywords:* Norbornene; ROMP; Organosoluble

## 1. Introduction

Interest in the metathesis reaction of functional olefinic derivatives containing functional groups and catalysts has increased over the recent years with the aim of obtaining polymer structures with attractive properties [1–5]. Recently, active polymers have found increased and wide demand such as in photoresists, coatings, and printing inks; however, there are a few example of functional metathesis polymeric materials that have been synthesized with polar active side chains such as cross-linkable (meth)acryloyl group [2,4–8]. Furthermore, the reactivity of the active side chain plays an important role in the preparation of polymeric network materials [2,4–8]. Cross-linkable polymers have found a wide demand in the domain of interpenetrating polymer networks, non-linear optical materials, macro- and microlithography, and the formation of more thermally and chemically resistant materials [9]. The development of polymers with cross-linkable end groups such as (meth)acryloyl group is one of interest for the preparation of interpenetrating polymer networks, AB cross-linked polymeric materials, and for the immobilization of biomaterials [1,2,4,6]. The high functional group tolerance of the 'Grubbs Catalyst' $RuCl_2(CHPh)[P(C_6H_{11})_3]_2$ (**A**) and $Ru(=CHPh)Cl_2[P(C_6H_{11})_3]L$ (L=1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (**B**) has promoted an investigation into the use of ROMP in the formation of functional polynorbornenes [1,2,4,10].



In this study, a series of functional norbornenes with differing α,β-unsaturated functional groups were prepared.

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The reactivity of ROMP of the functional norbornenes having (meth)acryloyl and cyclic norbornene groups using catalyst **A** or **B** as an initiator was investigated. The molecular structural effect of various monomer structures on ROMP and photo-initiated radical polymerization was also discussed.

## 2. Experimental

### *2.1. Synthesis of 5-[(methacryloyloxyethyl amino carboxylethoxy)carbonyl]bicyclo[2.2.1]hept-2-ene (**3a**) (Scheme 1)*

Synthesis of 5-(hydroxyethoxy carbonyl)bicyclo[2.2.1]-hept-2-ene (**2b**) (100 °C/5 mmHg) was accomplished via Diels–Alder reaction of cracked dicyclopentadiene and hydroxy ethyl acrylate (HEA) (**1b**). A mixture of cyclopentadiene (0.30 mmol) and **1b** (0.33 mmol) was dissolved in dichloromethane (30 mL), and the solution was refluxed at 45 °C for 24 h. The MOI was reacted with **2b** and then **3a** was obtained and purified by column chromatography [$SiO_2$, eluent: ethyl acetate(EA)/*n*-hexane = 3/1, twice] as a viscous, colorless liquid [*endo*/*exo* = 74/26, $^{1}H$ NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 5.63, 5.87 (cyclic, =C*H*, *endo*), 5.82 (cyclic, =C*H*, *exo*), 5.85, 5.32 (vinylic, –O(O)C–C($CH_3$)=C$H_2$), 1.65 (methyl, –O(O)C–C(C$H_3$)=$CH_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 17.4 ($C_{11}$), 28.4 ($C_{n6}$), 29.5 ($C_{x6}$), 39.3 ($C_{14}$), 40.9 ($C_{x5}$), 41.8 ($C_{n1}$), 42.5 ($C_{x1}$), 42.4 ($C_{n5}$), 45.0 ($C_{n4}$), 45.5 ($C_{x7}$), 45.9 ($C_{x4}$), 48.8 ($C_{n7}$), 61.6 ($C_{17}$), 61.9 ($C_{x18}$), 62.0 ($C_{n18}$), 62.8 ($C_{13}$), 125.1 ($C_{12}$), 131.6 ($C_{n3}$), 134.9 ($C_{x3}$), 135.3 ($C_{10}$), 136.9 ($C_{n2}$), 137.4 ($C_{x2}$), 155.7 ($C_{16}$), 166.4 ($C_9$), 173.7 ($C_{n8}$), 175.2 ($C_{x8}$)].

### *2.2. Synthesis of 5-(methacryloyloxyethyl amino carboxyl ethoxy carbonyl)-5-(methyl)-bicyclo[2.2.1]hept-5-ene (**3b**) (Scheme 1)*

Synthesis of 5-(hydroxyethoxy carbonyl)-5-(methyl)-bicyclo[2.2.1]hept-2-ene (**2c**) (85 °C/1 mmHg) was accomplished via Diels–Alder reaction of cracked dicyclopentadiene and hydroxyethyl methacrylate (HEMA) (**1c**). A mixture of cyclopentadiene (0.30 mmol) and **1c** (0.33 mmol) was dissolved in dichloromethane (30 mL), and the solution was refluxed at 45 °C for 24 h. The **3b** was obtained by the reaction of **2c** and MOI and purified by recrystallization from *n*-hexane, mp = 49 °C (by DSC) [*endo*/*exo* = 49/51, $^{1}H$ NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 6.06, 6.22 (cyclic, =C*H*, *endo*), 6.07 (cyclic, =C*H*, *exo*), 5.59, 6.10 (vinylic, –O(O)C–C($CH_3$)=C$H_2$), 5.08 (N–*H*, *endo*), 4.96 (N–*H*, *exo*), 1.93 (methyl, –O(O)C–C(C$H_3$)=$CH_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 18.19 ($C_{11}$), 24.1 ($C_{n19}$), 26.2 ($C_{x19}$), 37.5 ($C_{n6}$), 37.9 ($C_{x6}$), 40.2 ($C_{14}$), 42.5 ($C_{x1}$), 42.8 ($C_{n1}$), 46.7 ($C_{x7}$), 48.9 ($C_{n7}$), 49.6 ($C_{n5}$), 50.0 ($C_{x5}$), 50.3 ($C_{n4}$), 50.8 ($C_{x4}$), 62.2 ($C_{17}$), 62.5 ($C_{x18}$), 62.8 ($C_{n18}$), 63.5 ($C_{13}$), 126.0 ($C_{12}$), 133.4 ($C_{n3}$), 135.2 ($C_{x3}$), 135.9 ($C_{10}$), 137.8 ($C_{x2}$), 138.6 ($C_{n2}$), 156.0 ($C_{16}$), 167.2 ($C_9$), 177.2 ($C_{x8}$), 178.5 ($C_{n8}$)].

### *2.3. Synthesis of ester-containing 5-(acryloyl ethoxycarbonyl)-bicyclo[2.2.1]hept-2-ene (**4a**) (Scheme 1)*

Synthesis of 5-(chlorocarbonyl)-bicyclo[2.2.1]hept-2-ene (**2d**) was accomplished via Diels–Alder reaction of cracked dicyclopentadiene and acryloyl chloride (**1d**). A mixture of cyclopentadiene (0.30 mmol) and **1d** (0.33 mmol) was dissolved in dichloromethane (30 mL), and the solution was refluxed at 45 °C for 24 h. The **4a** was prepared by the reaction of **2d** and HEA. Purification by column chromatography ($SiO_2$, eluent: EA/*n*-hexane = 1/5) yielded pure **4a** as a viscous, colorless liquid [*endo*/*exo* = 95/5, $^{1}H$ NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 5.86, 6.12 (cyclic, =C*H*, *endo*), 6.11 (cyclic, =C*H*, *exo*), 6.13 (vinylic, –O(O)C–C*H*=$CH_2$), 5.82, 6.39 (vinylic, –O(O)C–CH=C$H_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 29.0 ($C_{n6}$), 30.1 ($C_{x6}$), 41.4 ($C_{x1}$), 42.3 ($C_{n1}$), 42.8 ($C_{x5}$), 43.0 ($C_{n5}$), 45.5 ($C_{n4}$), 46.1 ($C_{x7}$), 46.4 ($C_{x4}$), 49.4 ($C_{n7}$), 61.6, 62.1 ($C_{n13}$, $C_{n14}$), 61.8, 62.0 ($C_{x13}$, $C_{x14}$), 127.8 ($C_{10}$), 131.1 ($C_{12}$), 132.1 ($C_{n3}$), 135.5 ($C_{x3}$), 137.6 ($C_{n2}$), 137.9 ($C_{x2}$), 165.6 ($C_9$), 174.2 ($C_{n8}$), 176.0 ($C_{x8}$)].

### *2.4. Synthesis of ester-containing 5-(methacryloylethoxycarbonyl)-bicyclo[2.2.1]hept-2-ene (**4b**) (Scheme 1)*

The **4b** was prepared by the reaction of **2d** and HEMA. Purification by column chromatography ($SiO_2$, eluent: EA/*n*-hexane = 1/9, twice) yielded pure **4b** as a viscous, colorless liquid [*endo*/*exo* = 90/10, $^{1}H$ NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 5.90, 6.18 (cyclic,=C*H*, *endo*), 6.11 (cyclic, =C*H*, *exo*), 1.96 (methyl, –O(O)C–C(C$H_3$)=$CH_2$), 5.60, 6.13 (vinylic, –O(O)C($CH_3$)=C$H_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 18.3 ($C_{11}$), 29.2 ($C_{n6}$), 30.4 ($C_{x6}$), 41.7 ($C_{x1}$), 42.6 ($C_{n1}$), 43.1 ($C_{x5}$), 43.3 ($C_{n5}$), 45.7 ($C_{n4}$), 46.4 ($C_{x7}$), 46.7 ($C_{x4}$), 49.6 ($C_{n7}$), 62.1, 62.2 ($C_{n13}$, $C_{n14}$), 61.9, 62.5 ($C_{x13}$, $C_{x14}$), 125.9 ($C_{10}$), 132.4 ($C_{n3}$), 135.7 ($C_{x3}$), 136.0 ($C_{12}$), 137.8 ($C_{n2}$), 138.1 ($C_{x2}$), 167.0 ($C_9$), 174.4 ($C_{n8}$), 175.9 ($C_{x8}$)].

### *2.5. Synthesis of ester-containing 5-(acryloyl methyl) bicyclo[2.2.1]hept-2-ene (**5a**) (Scheme 1)*

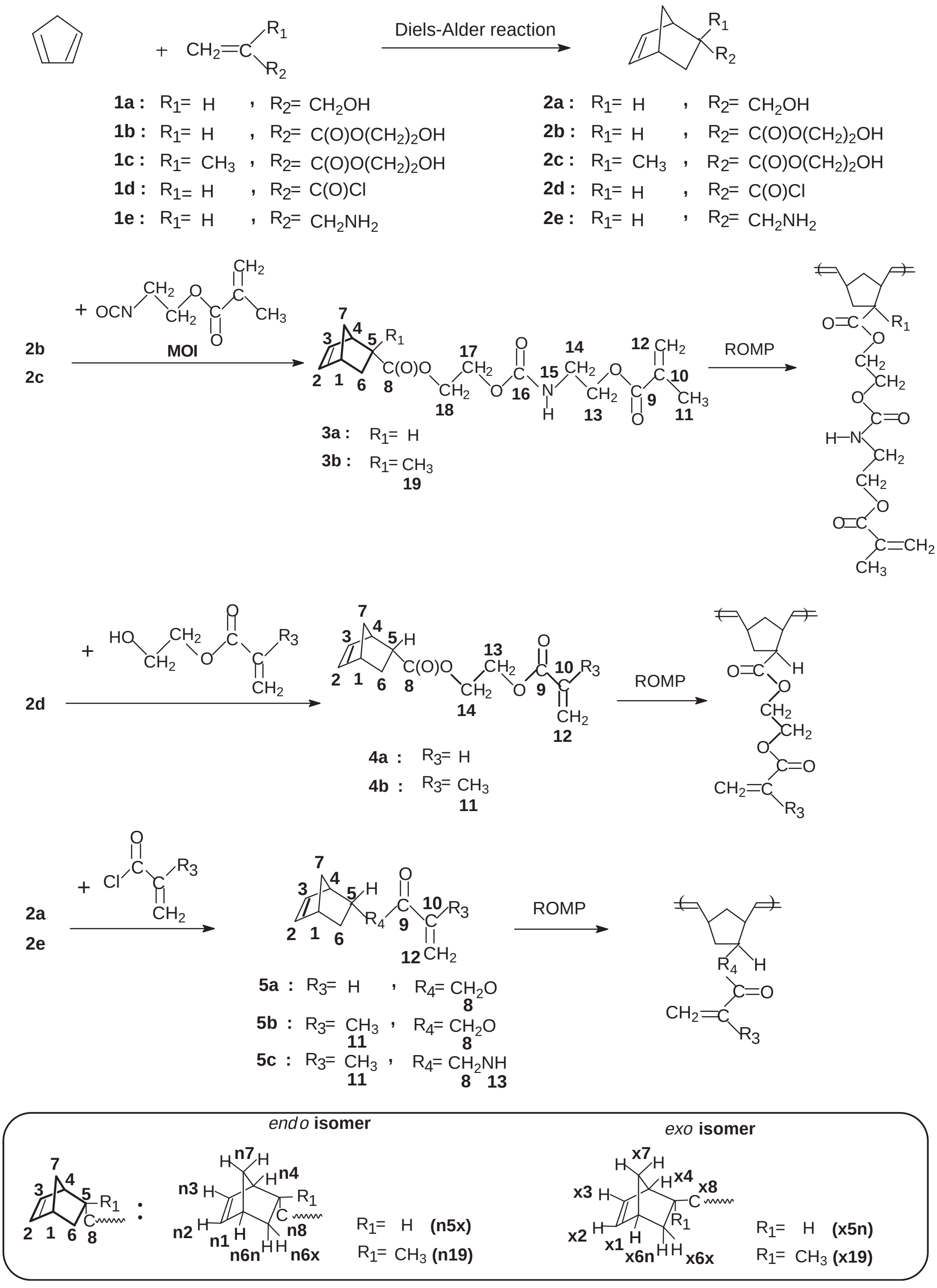
The **5a** was prepared by the reaction of **2a** and **1d** and purified by column chromatography ($SiO_2$, eluent: EA/*n*-hexane = 1/5) as a viscous, colorless liquid (89–91 °C/7 mmHg) [*endo*/*exo* = 84/16, $^{1}H$ NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 5.91, 6.11 (cyclic,=C*H*, *endo*), 6.05 (cyclic,=C*H*, *exo*), 6.12 (vinylic, –O(O)C–C*H*=$CH_2$), 5.78, 6.37 (vinylic, –O(O)C–CH=C$H_2$); $^{13}C$ NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 28.8 ($C_{n6}$), 29.4 ($C_{x6}$), 37.7 ($C_{n5}$), 37.9 ($C_{x5}$), 41.5 ($C_{n1}$), 42.1 ($C_{x1}$), 43.5 ($C_{x4}$), 43.7 ($C_{n4}$), 44.8 ($C_{x7}$), 49.2 ($C_{n7}$), 67.8 ($C_{n8}$), 68.4 ($C_{x8}$), 128.5 ($C_{10}$), 130.3 ($C_{12}$), 132.0 ($C_{n3}$), 136.1 ($C_{x3}$), 136.8 ($C_{x2}$), 137.4 ($C_{n2}$), 166.0 ($C_{n9}$), 166.1 ($C_{x9}$)].

### *2.6. Synthesis of ester-containing 5-(methacryloyl methyl) bicyclo[2.2.1]hept-2-ene (**5b**) (Scheme 1)*

The **5b** was prepared by the reaction of **2a** and methacryloyl chloride and obtained as a colorless liquid following distillation under reduced pressure (89–91 °C/4 mmHg) [*endo*/*exo* = 85/15, $^1$H NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 6.00, 5.94 (=C*H*, cyclic, *endo*), 5.97 (=C*H*, *exo*), 5.77, 5.99 (=C*H*, 2H, vinylic); $^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 17.1 ($C_{11}$), 27.8 ($C_{n6}$), 28.5 ($C_{x6}$), 36.9 ($C_{n5}$), 37.1 ($C_{x5}$), 40.7 ($C_{x4}$), 40.8 ($C_{n1}$), 42.9 ($C_{x1}$), 43.1 ($C_{n4}$), 44.5 ($C_{x7}$), 48.7 ($C_{n7}$), 67.4 ($C_{n8}$), 68.1 ($C_{x8}$), 125.3 ($C_{12}$), 136.8 ($C_{n3}$), 136.9 ($C_{x3}$), 137.2 ($C_{n2}$), 137.4 ($C_{x2}$), 137.8 ($C_{10}$), 167.9 ($C_9$)].

### 2.7. Synthesis of amide-containing 5-(methacryloyl amino methyl)bicyclo[2.2.1] (5c) (Scheme 1)

Synthesis of 5-(amino methyl) bicyclo[2.2.1] hept-2-ene (**2e**) (bp = 60–61 °C/11 mmHg) was accomplished via the Diels–Alder reaction of freshly cracked cyclopentadiene and allyl amine(**1e**) [5]. The **5c** was prepared by the reaction of **2e** and methacryloyl chloride and purified by recrystallization



Scheme 1. Synthesis and ROMP of various functional norbornenes with different α,β-unsaturated functional groups.

from *n*-hexane, mp = 96 °C (by DSC) [*endo*/*exo* = 85/15, $^1$H NMR (500 MHz, $CDCl_3$), $\delta$ (ppm): 6.17, 5.97 (=C*H*, cyclic, *endo*), 6.06 (=C*H*, *exo*), 6.46 (N–*H*, *endo*), 6.51 (N–*H*, *exo*), 5.66, 5.31 (vinylic, $-O(O)C-C(CH_3)=CH_2$); $^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 17.6 ($C_{11}$), 29.1 ($C_{n6}$), 29.8 ($C_{x6}$), 40.8 ($C_{n5}$), 40.9 ($C_{x5}$), 41.5 ($C_{x4}$), 41.6 ($C_{n1}$), 42.9 ($C_{n4}$), 43.4 ($C_{x1}$), 43.5 ($C_{n7}$), 44.3 ($C_{x7}$), 44.4 ($C_{x8}$), 48.7 ($C_{n8}$), 119.2 ($C_{12}$), 132.5 ($C_{n3}$), 136.6 ($C_{x3}$), 137.1 ($C_{x2}$), 137.9 ($C_{n2}$), 140.7 ($C_{10}$), 169.5 ($C_9$)].

### 2.8. Ring-opening metathesis polymerization

The active polynorbornenes with functional groups were obtained by ROMP using catalysts **A** and **B** as previously reported [5,6].

### 2.9. Free radical photopolymerization

Photopolymerization was carried out using 2,2′-azobis(cyclohexane-1-nitrile) as an initiator at 30 °C, using an Ushio 250 W high-pressure mercury lamp together with filters (Toshiba UV-DIC and IRQ-80) for 3650 Å [11].

### 2.10. Synthesis of AB cross-linked systems of poly(**5b**) and polyMMA

The monomer **5b** was dissolved in 4 mL of methylene chloride and added to the catalyst solution [catalyst **A** in methylene chloride]. After ring-opening metathesis polymerization (30 °C, 2 h), the solvent and MMA were completely removed by evaporation under reduced pressure, and a fixed amount of MMA was injected into the reactor to dissolve poly(**5b**). Benzoyl peroxide, 1% (w/w) based on MMA was added to the polymer solution as a free radical initiator. The weight ratio of poly(**5b**) to methyl methacrylate are 5, 10 and 15% (w/w) based on MMA. The solution of poly(**5b**) and MMA was degassed thrice via a freeze–pump–thaw cycle, then heated at 90 °C for 16 h. The MMA polymerized and cross-links were formed simultaneously with poly(**5b**) [6].

### 2.11. Instruments

$^1$H 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. Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights 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, $10^3$, $10^4$, $10^5$ Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 mL $min^{-1}$) as the eluent. The eluents were monitored with RI detector and UV detector (Gilson model 116) at 254 nm.

## 3. Results and discussion

### 3.1. Molecular architecture on miscellaneous organo-soluble polynorbornenes with active side chains by using catalysts **A** (***P1–P10***, Table1) and **B** (***P11–P26***, Table 2)

Organo-insoluble precipitates were obtained when ring-opening metathesis polymerization (ROMP) of **5c** (Scheme 1) containing α,β-unsaturated amide group was performed using catalyst **A**(**P10**). In the IR spectrum of poly(**5c**), N–H stretching of the amide group appeared near 3030–3330 $cm^{-1}$ and C=O stretching vibration appeared near 1600–1640 $cm^{-1}$ because of hydrogen bonding shift [Fig. 1(A)] [12]. To improve the solubility of the polymer, except for heating the sample and adding a hydrogen-bonding breaking solvent, preparation of a random copolymer was considered to be a strategy, which expected to decrease the level of hydrogen bonding between the two amide groups. The bicyclo[2.2.1]hept-2-ene (NB) was employed as a candidate of comonomer. ROMP of NB and **5c** (molar ratio of NB:**5c** = 1:1) was carried out to prepare an active random poly(NB-*co*-**5c**), which was soluble in $CH_2Cl_2$, $CHCl_3$, benzene, xylene, toluene, and THF. In $^1$H NMR spectrum of poly(NB-*co*-**5c**), the vinylic proton peaks of the methacryloyl group appeared between $\delta$ 5.23 and 5.60 ppm, the signals of vinylic protons of the polynorbornene main chains appeared between $\delta$ 5.20 and 5.51 ppm, and the signals of the amino protons of the amide group appeared between $\delta$ 4.80 and 5.10 ppm. The signals of vinylic carbons of methacrylol group at $\delta$ 126.0 and 136.0 ppm and methyl carbon of methacrylol group at $\delta$ 18.3 ppm could be observed. In the IR spectrum of poly(NB-*co*-**5c**), the N–H stretching near 3030–3330 $cm^{-1}$

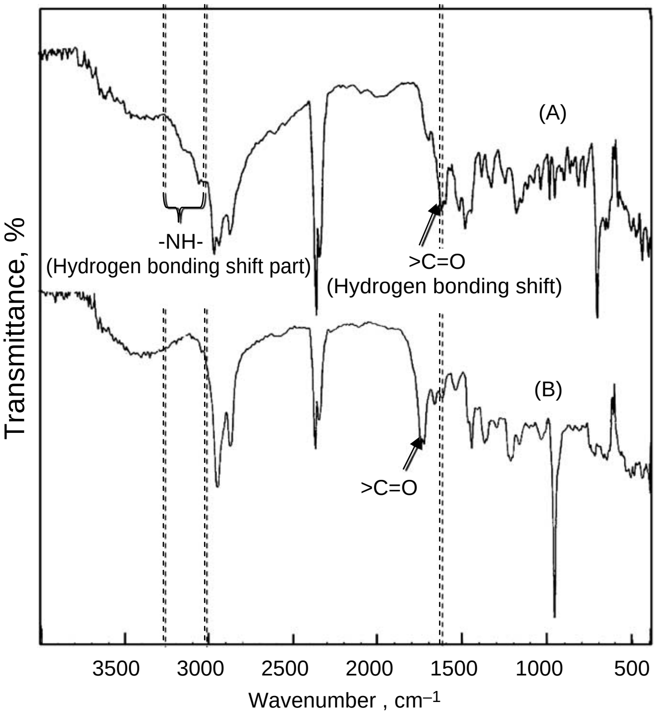
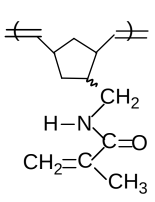
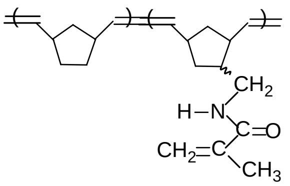


Fig. 1. FT-IR spectra of functional polynorbornenes: (A) poly(**5c**) and (B) random poly(NB-*co*-**5c**).

disappeared and one N–H stretching vibration near 3500 cm$^{-1}$ was observed, indicating that the hydrogen bonding had been disturbed and almost disappeared [Fig. 1(B)][12].



**Poly(5c)**



**Random poly(NB-*co*-5c)**

ROMP of **5b** with [monomer]/[catalyst] ratio, [M]/[C] = $10^3$ was successfully carried out and poly(**5b**) with high molecular weight of $3.1\times10^4$ was obtained (**P9**) [4–8]. The poly(**5b**) was soluble in dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), $CH_2Cl_2$, $CHCl_3$ and THF. Similarly, an organo-soluble poly(**5a**) with a high molecular weight of $4.3\times10^4$ was obtained (**P8**). Poly(**5a**) contained more *trans* olefins (trans/cis = 86/14) while poly(**5a**) synthesized by **B** had a slight excess of *cis* olefin (trans/cis = 48/52) (**P23** and **P24**).

Polynorbornenes derived from active norbornenes with ethylene between urethane group and ester group such as **3a**,**b** showed excellent solubility. Polymerization of **3a**,**b** led to the formation of a highly organo-soluble polynorbornene with active side chains [poly(**3a,b**)] (Scheme 1). Gel formation did not occur during the polymerization of **3a**,**b** with catalyst **A**. The molecular weight of the poly(**3a**) was high ([M]/[C] = $10^3$, $\bar{M}_n = 2.5\times10^5$ and $\bar{M}_w/\bar{M}_n = 1.6$) with narrow molecular weight distribution. Poly(**3a**) showed excellent solubility in DMSO, DMF, DMAc, THF, pyridine, $CH_2Cl_2$ and $CHCl_3$. Similarly the molecular weight of the poly(**3b**) was high ([M]/[C] = $1.5\times10^4$, $\bar{M}_n = 1.1\times10^5$ and $\bar{M}_w/\bar{M}_n = 1.7$) with narrow molecular weight distribution. When $CH_2Cl_2$ was used as a solvent and **B** ($2.45\times10^{-5}$ mol L$^{-1}$) was used as a catalyst, gel formation was observed within 5 min at 30 °C during ROMP of **3b** with [M]/[C] of $3\times10^2$ (**P15**). Interestingly, enhancing [M]/[C] could be a strategy to obtain high molecular weight poly(**3b**) and avoid gelation. For example, ROMP of **3b** with [M]/[C] of $2\times10^4$ was performed using catalyst **B** ($1.12\times10^{-5}$ mol L$^{-1}$) at 30 °C (**P16**). An organo-soluble poly(**3b**) could be obtained with a high molecular weight of $5.0\times10^5$ and PDI of 4.1 (**P16**). The polydispersity indice (PDI) ($\bar{M}_w/\bar{M}_n$) of poly(**3b**) obtained from ROMP under catalyst **B** catalyzed condition was broad (PDI = 4.1) (**16**), which arises from an unfavorable rate of initiation relative to propagation as well as considerable secondary metathesis (‘back-biting’) [13,14]. That is, catalyst **B** is an effective polymerization catalyst, the rate of propagation is much higher than the rate of initiation leaving a high concentration of uninitiated carbene available upon complete monomer consumption, resulting in non-living behavior and broad PDI [13,14].

Table 1
Molecular architecture effect of various norbornenes with different α,β-unsaturated functional groups on number-averaged molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) in the ring-opening metathesis polymerization by using catalyst **A**

| Polymer code | Monomer | [M]/[C][a] | $\bar{M}_n$[b] | $(\bar{M}_w/\bar{M}_n)$[b] |
|---|---|---|---|---|
| **P1** | **3a** | $10^3$ | $2.5\times10^5$ | 1.6 |
| **P2** | **3b** | $10^3$ | $<10^{3c}$ | – |
| **P3** | **3b** | $1.5\times10^4$ | $1.1\times10^{5c}$ | 1.7 |
| **P4** | **4a** | $10^3$ | $<10^{3c}$ | – |
| **P5** | **4a** | $5\times10^3$ | $5.0\times10^{3c}$ | 1.8 |
| **P6** | *exo*-**4a** | $10^3$ | $1.0\times10^{5c}$ | 2.0 |
| **P7** | **4b** | $10^3$ | $<10^{3c}$ | – |
| **P8** | **5a** | $10^3$ | $4.3\times10^{4d}$ | 2.1[d] |
| **P9** | **5b** | $10^3$ | $3.1\times10^{4d}$ | 2.2[d] |
| **P10** | **5c** | $10^3$ | Insoluble elastomer | – |

[a] Experimental conditions: catalyst **A** ($2.5\times10^{-3}$ mmol); methylene chloride (4 mL); temperature: 30 °C; polymerization time: 2 h; [M]/[C]:[monomer]/[catalyst] ratio.

[b] Molecular weight determined by GPC (polystyrene was used as a standard).

[c] The yield is less than 1%.

[d] Experimental conditions: catalyst **A** ($2.5\times10^{-3}$ mmol) after ligand exchange with 1-pentene; methylene chloride (4 mL); temperature: 30 °C.

ROMP of **3a** and **3b** (Scheme 1) was carried out using catalyst **A** at 30 °C. Poly(**3a**) with a molecular weight of $2.5\times10^5$ being obtained with the yield of 60% (**P1**). However, the yield of poly(**3b**) was low even after 24 h polymerization (**P2**), which might have been due to the steric effect of 5-substituted methyl group in the structure of **3b**. An organo-soluble poly(**3b**) with high molecular weight of $1.1\times10^5$ (PDI = 1.7) (**P3**) was obtained. ROMP of **3a** and **3b** was performed using catalyst **B** at 55 °C. Gelation occurred after 2 min during ROMP with various [M]/[C] even high [M]/[C] of $10^4$ (**P12** and **P14**). After shorten the reaction time to 1 min, an organo-soluble poly(**3a**) and poly(**3b**) with a high molecular weight can be obtained (**P11** and **P13**). ROMP of **4a** with predominant *endo* isomer(*endo*/*exo* = 95/5) and without 5-substituted methyl group had been studied. The yield of poly(**4a**) was less than 1% and only an oligomer of poly(**4a**) with a molecular weight of $5.0\times10^3$ (**P5**) was obtained using catalyst **A**, which might have been due to predominant *endo* isomer (*endo*/*exo* = 95/5) although **4a** contains the carboxyl group. Similarly, it is difficult to polymerize **4b** with the 5-substituted methyl group using catalyst **A** (**P7**). ROMP of **4a** with [M]/[C] of $10^4$ was performed by using more active catalyst **B** ($4.2\times10^{-5}$ mol L$^{-1}$ in THF solution) at 55 °C (**P17**). After 20 min of reaction time, an organo-soluble poly(**4a**) was obtained with a high molecular weight of $2.9\times10^4$ (predominant cis) and PDI of 1.7 (**P17**). Pure *exo*-**4a** (Scheme 2) was also prepared and poly(*exo*-**4a**) with high molecular weight of $10^5$ (PDI = 2.0) was obtained using **A** (**P6**). Also, ROMP of *exo*-**4a** with [M]/[C] of $10^4$ was performed using catalyst **B** ($4.2\times10^{-5}$ mol L$^{-1}$ in THF solution) at 55 °C (**P18**). After 5 min of reaction time, an organo-soluble poly(*exo*-**4a**) was obtained with a high molecular weight of $3.6\times10^4$ and PDI of 2.5 (**P18**). When *endo* rich **4a** was subjected to ROMP, it was observed that the reactivity of

Table 2
Molecular architecture effect of various norbornenes with different α,β-unsaturated ester and amide on number-averaged molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) in the ring-opening metathesis polymerization by using catalyst **B**

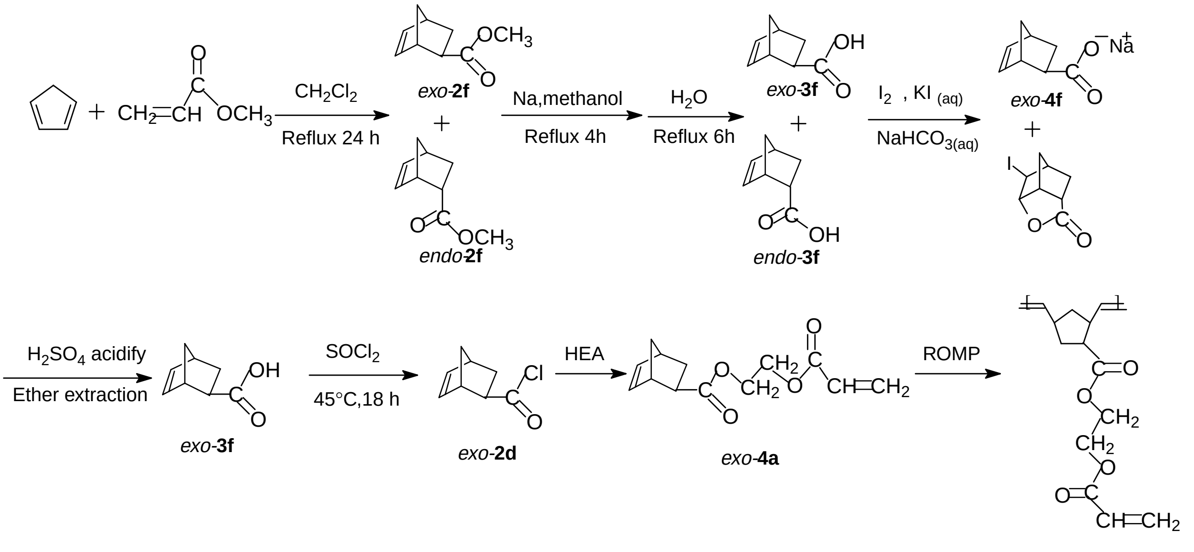
| Polymer code | Monomer | [M]/[C][a] | Temperature (°C) | Time (min) | Solvent | $\bar{M}_n$[b] | ($\bar{M}_w/\bar{M}_n$)[b] |
|---|---|---|---|---|---|---|---|
| **P11** | **3a** | $10^4$ | 55 | 1 | THF | $3.4\times10^5$ | 3.6 |
| **P12** | **3a** | $10^4$ | 55 | 2 | THF | Gelation[c] | Gelation[c] |
| **P13** | **3b** | $10^4$ | 55 | 1 | THF | $4.3\times10^4$ | 2.9 |
| **P14** | **3b** | $10^4$ | 55 | 2 | THF | Gelation[c] | Gelation[c] |
| **P15** | **3b** | $3\times10^2$ | 30 | 5 | $CH_2Cl_2$ | Gelation[c] | Gelation[c] |
| **P16** | **3b** | $2\times10^4$ | 30 | 10 | $CH_2Cl_2$ | $5.0\times10^5$ | 4.1 |
| **P17** | **4a** | $10^4$ | 55 | 20 | THF | $2.9\times10^4$ | 1.7 |
| **P18** | *exo*-**4a** | $10^4$ | 55 | 5 | THF | $3.6\times10^4$ | 2.5 |
| **P19** | **4b** | $10^4$ | 55 | 1 | THF | $7.4\times10^4$ | 6.7 |
| **P20** | **4b** | $10^4$ | 45 | 5 | THF | $3.3\times10^4$ | 1.8 |
| **P21** | **4b** | $10^4$ | 45 | 120 | THF | $3.3\times10^4$ | 1.8 |
| **P22** | **5a** | $10^4$ | 55 | 5 | THF | $4.3\times10^4$ | 1.6 |
| **P23** | **5a** | $2\times10^4$ | 30 | 10 | $CH_2Cl_2$ | $7.2\times10^4$ | 2.1 |
| **P24** | **5a** | $2\times10^4$ | 30 | 60 | $CH_2Cl_2$ | $4.7\times10^4$ | 6.4 |
| **P25** | **5b** | $10^4$ | 45 | 10 | THF | $8.7\times10^4$ | 1.7 |
| **P26** | **5b** | $2\times10^4$ | 55 | 1 | THF | $6.2\times10^4$ | 2.1 |

[a] [M]/[C]:[monomer]/[catalyst] ratio.
[b] Molecular weight determined by GPC (polystyrene was used as a standard).
[c] Gel formation during the polymerization.

*exo*-**4a** isomer was significantly higher than the *endo* rich **4a** isomer [13,14].

### 3.2. Free radical photopolymerization of novel multiply polymerizable functional norbornene derivatives

Rates of photopolymerization of novel multiple polymerizable norbornene derivatives in different solvents with varying dielectric constant were determined by dilatometry [11]. Interestingly, the results of photopolymerization of all monomers had shown that there is an existence of a critical time ($t_c$) for the cross-linking reaction and the insoluble cross-linked microgel was obtained after a period of UV irradiation, which might have been due to the free radical reaction of norbornene group and (meth)acrylic group of multiply polymerizable norbornene derivatives [15,16]. From Fig. 2, although the volume contraction (%) of the starting cross-linking reaction was calculated to be smaller than $1\times10^{-3}\%$, $t_c$ values of **5b** and **3b** are observed within 4 and 7 mins, respectively. Sen et al. and Sveum et al. also reported that the norbornene group could possibly react with the (meth)acrylic group under free radical mediated polymerization condition although the free radical reaction could not be carried out efficiently [15,16]. In this study, insoluble cross-linked microgel was obtained when photopolymerization of **3b** (0.25 mol $L^{-1}$) occurred in *N*,*N*-dimethylformamide (DMF) over 7 mins of UV irradiation (Fig. 2). Before commencing the cross-linking reaction time (time < $t_c$), the relationship of the volume contraction to the reaction solution and irradiation time was linear. From the contraction of volume of the reaction mixture prior to the onset of the cross-linking reaction, the initial rate of photopolymerization was calculated (Table 3)



Scheme 2. Synthesis and ROMP of an *exo*-norbornene with ester group (*exo*-**4a**).

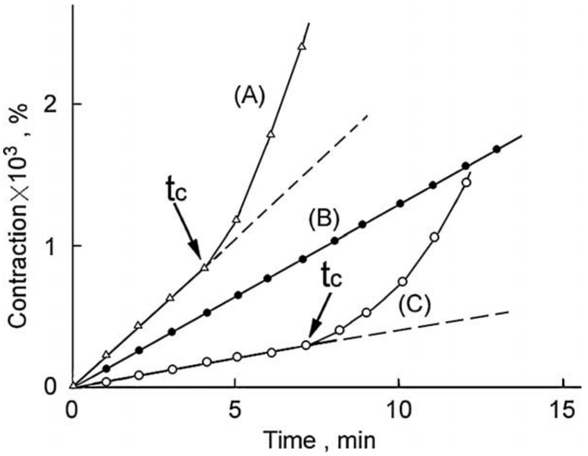


Fig. 2. Contraction of volume of the reaction mixture during free radical photopolymerization of the multiply polymerizable norbornene derivatives (A) **5b**, (B) MMA, and (C) **3b** under UV irradiation.

[14]. Following the occurrence of the cross-linking reaction (time $>t_c$), the contraction of volume of the reaction solution increased remarkably. Similarly, the initial rates of photopolymerization in various solvents, concentrations and monomers were summarized in Table 3 [11]. Comparing the slopes of the volume contraction curves of **3b**, methyl methacrylate (MMA) and **5b**, the rate of photopolymerization of various monomers is in the following order: **5b** > MMA > **3b** (before $t_c$) (Fig. 2).

From Table 3, it can be seen that the rate of photopolymerization ($R_p$) of **3b** in less polar solvents such as benzene is higher than that of **3b** in polar solvents such as DMF (Runs no. 8 and 11, Table 3). The influence of the solvent on the rate of photopolymerization ($R_p$) might be explained in terms of the difference in the environment around the propagating radical of the polymer chain and monomer. As the polarity of the solvent increases, there will be effective hydrogen-bonding between the monomer and solvent. Since, the polar solvent might readily interact with the propagating polymer chain and/or monomer (for example, hydrogen-bonding) in the propagation stage and thus probably lead to the dormant condition of the propagating polymer chain and/or monomer. This may be the reason for observing a lower rate of polymerization ($R_p$) in polar solvent [17,18]. As the rate of polymerization ($R_p$) is dependent on the polarity of solvent, the dielectric constant ($\varepsilon$) of the solvent may be used as a rough measure of such interactions (Table 3). The lower rate of polymerization ($R_p$) of functional norbornenes such as **5c**, **3a** and **3b** having more polar groups like urethane or amide group than MMA in more polar solvents clearly demonstrates the dormant stage of propagation due to the hydrogen-bonding of those monomers (Runs no. 7–9, Table 3). This also further confirms the existence of strong interactions between the solvent molecule and the monomer, and/or the propagating polymer chain, which contains more polar urethane or amide group by hydrogen bonding [17,18]. The lowest rate of polymerization ($R_p$) was observed for **5c** with amide group in DMF. This behavior might be due to the hydrogen-bonding between **5c** and/or propagating poly(**5c**) chain and solvent molecule. When comparing the UV spectra of **5c** and **3b** in DMF solution, the remarkable red shift of $\lambda_{max}$ by 14 nm from 272 nm (**3b**) to 286 nm (**5c**) can be observed. These results clearly demonstrate that the ability of amide-containing **5c** to exhibit stronger hydrogen bonding than those having ethylene unit between urethane and ester groups, such as **3a** and **3b**. Furthermore, the rate of polymerization ($R_p$) of **5a** without the methyl group at $\alpha$-carbon (Run no. 2) is higher than that of **5b** with the methyl group (Run no. 5) (Table 3). Similar behavior was observed in the polymerization of methyl acrylate (MA) and methyl methacrylate (MMA), even in polar solvents such as DMF (Runs no. 3 and 6, Table 3). The rates of polymerization ($R_p$) of **4a** and **5a** are higher than that of MA (Run no. 3, Table 3) and these behaviors might be due to the bulky effect of the norbornene group, which is present in the side chain on the kinetics of the termination stage [19,20]. The rate of photopolymerization ($R_p$) of **4b** (Run no. 4) and **5b** (Run no. 5) are higher than that of MMA (Run no. 6) (Table 3), indicating that the steric effect of the bulky ester norbornene group is important. In this work, alkyl methacrylate with a bulky norbornene ester substituent such as **4b** and **5b** were prepared and the effect of size of substituent on the rate of free radical polymerization was investigated. It was found that the introduction of the bulky ester groups, particularly the norbornene group (**4b** and **5b**), increased its polymerization rate, compared with MMA (Run no. 6, Table 3). It was ascribed to decrease in the termination rate of alkyl methacrylate with a bulky norbornene ester substituent (such as **4b** and **5b**), resulting in an increase in the concentration of its propagating radical at a stationary state. In contrast to this, although the bulky amide group, such as norbornene amide group (such as **5c** and Run no. 9, Table 3), was introduced, however, the rate of free radical polymerization was decreased in comparison with methyl methacrylate (MMA) (Run no. 6, Table 3). This behavior was attributed to the hydrogen bonding of the amide group resulting in the formation of a dormant propagating polymer chain and/or monomer in the propagating stage of free radical photopolymerization [17,18]. In the IR spectrum of **5c**,

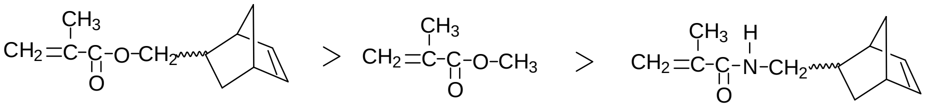
Table 3
Structure and solvent effect on photopolymerization of novel norbornene derivatives

| Runs no. | Monomer | Solvent | $\varepsilon$[a] | $R_p\times10^6$ (mol L$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|
| 1 | **4a** | DMF | 36.1 | 30.41 |
| 2 | **5a** | DMF | 36.1 | 12.73 |
| 3 | MA | DMF | 36.1 | 9.27 |
| 4 | **4b** | DMF | 36.1 | 7.95 |
| 5 | **5b** | DMF | 36.1 | 5.67 |
| 6 | MMA | DMF | 36.1 | 4.70 |
| 7 | **3a** | DMF | 36.1 | 3.37 |
| 8 | **3b** | DMF | 36.1 | 2.81 |
| 9 | **5c** | DMF | 36.1 | 1.47 |
| 10 | MMA | Benzene | 2.3 | 5.11 |
| 11 | **3b** | Benzene | 2.3 | 4.17 |

Experiment conditions: [2,2′-azobis(cyclo hexane carbonitrile)] $=3.0\times10^{-3}$ mol L$^{-1}$; [monomer] $=0.2$ mol L$^{-1}$; temperature (30 °C), by dilatometer method.

[a] Dielectric constant.

the N–H stretching could be observed as multiple bands near 3300 $\text{cm}^{-1}$ and this confirmed the existence of hydrogen bonding. The rates of free radical polymerization for various monomers having bulky ester and amide groups are in the following order:



**5b** (Higher $R_p$) MMA **5c** (Lower $R_p$)

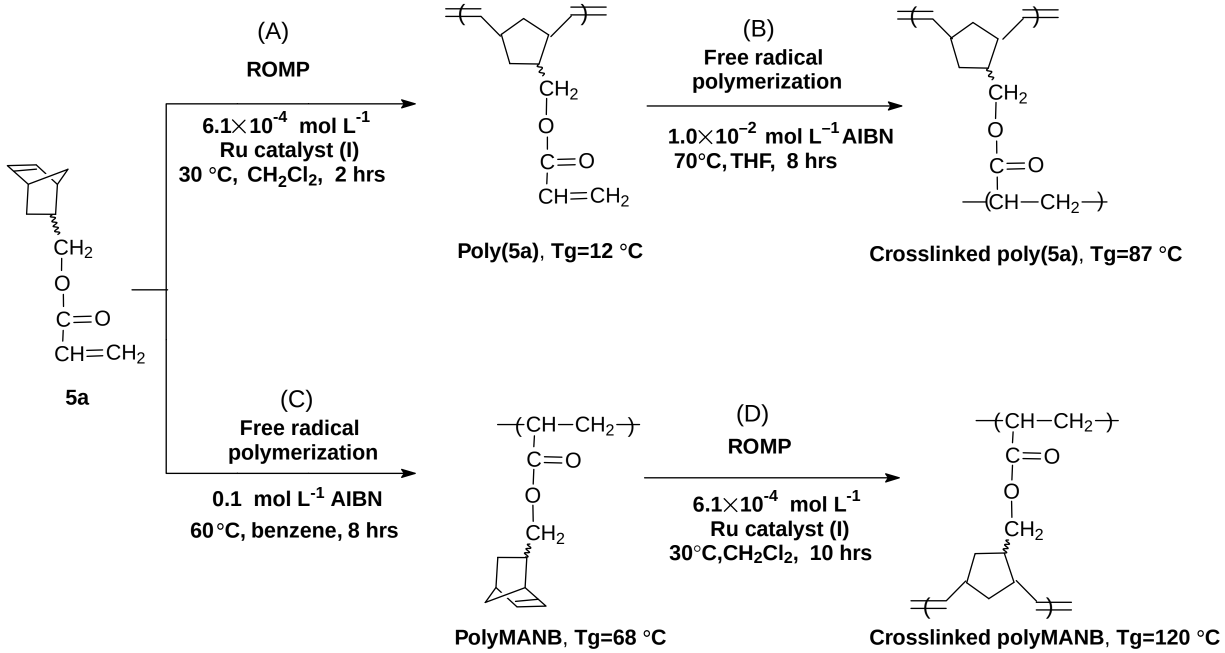
These behaviors are similar to the previous results reported from Otsu et al. and Liaw et al. [19,20]. The rates of free radical polymerization for various monomers having bulky ester and urea groups are in the following order: alkyl methacrylate with adamantly ester substituent (AdMAI) (the highest $R_p$) > alkyl methacrylate with cyclohexyl ester substituent (CHMA) > MMA > alkyl methacrylate with a bulky adamantyl urea (AdMAI) (the lowest $R_p$) [19,20]. The bands near 3256 $\text{cm}^{-1}$ due to N–H stretching in the IR spectrum of AdMAI confirmed the existence of hydrogen bonding [19,20].

### 3.3. Dual cure applications by using monomer 5a

Novel polymer architectures were prepared from difunctional **5a** by dual cure. It was possible to carry out ring-opening metathesis polymerization and conventional free radical polymerization of **5a** as it contains a norbornene group and an acryloyl group. A novel organo-insoluble functional polynorbornene could be obtained after ROMP of **5a** [Scheme 3 (A)]. The resulting functional polynorbornene, poly(**5a**), still contains cross-linkable side chains and shows a glass transition temperature ($T_g$) value of 12 °C. Furthermore, poly(**5a**) was cross-linked by thermal free radical polymerization [Scheme 3 (B)]. Glass transition temperature ($T_g$) of the resulting cross-linked poly(**5a**) was observed at 87 °C. Also, an intended polymer with norbornene side chains [poly(MANB)] has been prepared [Scheme 3 (C)]. Additional cross-linking was observed because of the norbornene-containing side chains of the poly(MANB) ($T_g$ = 68 °C). The resulting cross-linked poly(MANB) was insoluble in common organic solvents and had a $T_g$ value at 120 °C [Scheme 3 (D)].

### 3.4. Application of AB cross-linked polymeric materials of poly(5b) and polyMMA

Despite the many current industrial applications of polyMMA, there are problems with thermal stability, and chemical resistance. By polymerizing MMA in the presence of poly(**5b**), cross-links should be formed with methacyoyl side chains of the poly(**5b**), cross-links should be formed with methacryloyl side chains of the poly(**5b**), thus yielding AB cross-linked polymeric material. In accordance with the AB cross-linked polymer, the material was found to be insoluble in benzene, toluene, chloroform and methylene chloride, indicating that such materials has highly chemical resistance. 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 Table 4, the thermal stability of interpenetrating (IPN) polymer of polyMMA and poly(**5b**) was higher than that of pure polyMMA. Increase in thermal



Scheme 3. Cascades of ROMP and radical polymerization.

Table 4
Comparison of thermal decomposition for the new AB cross-linked materials of poly(**5b**) with polyMMA

| wt% of poly(**5b**) used in cross-linking reaction | $T_{d,10\%}$ (°C)[a] |
|---|---|
| 0% (100% PolyMMA) | 250 |
| 5% (95% PolyMMA) | 282 |
| 10% (90% PolyMMA) | 308 |
| 15% (85% PolyMMA) | 355 |

[a] All values are obtained under an atmosphere of nitrogen at a scan rate of 20 °C $\min^{-1}$.

stability of 32 °C [5% poly(**5b**)], 58 °C [10% poly(**5b**)], and 105 °C [15% poly(**5b**)] were observed for the new materials relative to pure polyMMA (Table 4).

## 4. Conclusion

A series of functional norbornenes were prepared. Organo-insoluble elastomers were obtained by ROMP of some derivatives due to the hydrogen bonding of amide groups. No gelation and/or insoluble elastomer formation occurred during ROMP of **3a**,**b** with catalyst **A** because the ethylene between the urethane group and ester group of poly(**3a**,**b**) enhanced solubility. High performance polynorbornenes with cross-linkable groups could be designed with high potential for practical application.

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