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Syntheses of Novel Polynorbornene Derivatives via Ring Opening Metathesis Polymerization

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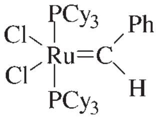
Summary: Ring opening metathesis is an important class of controlled polymerization techniques. Synthesis of novel polynorbornene derivatives with functional groups designed for application in crosslikable and self assembling materials, and the polymerizations via ROMP and/or free radical polymerization are introduced. Novel monomers and/or macroinitiators for combination of two polymerization techniques are useful for controlling molecular architecture. The sequence of using controlled polymerization techniques affects the molecular structure and the properties of resulting polymers.

Keywords: ATRP; crosslinkable; polynorbornene; ROMP; self-assembling

Introdction

Since 1991 Nippon Zeon has produce the polymer Zeonex® with saturated C=C bond in the backbone. Increasing interest in the metathesis reaction of functional olefinic derivatives containing functional groups and catalysts has developed over recent years with the aim of obtaining polymer structures with attractive properties.[1–5] The strained cycloolefin polymers via ROMP, such as norbornene derivatives, are known for their large applications due to the high transparency, chemical resistance, and electric properties.[2] Recently, active polymers have found increased and wide demand such as in photoresists, coatings, printing inks, molding, adhesive, emulsifiers, dispersion stabilizer, compatibilizers and drug delivery; however there are only a few example of functional metathesis polymeric materials that have been synthesized with polar active side chains such as cross-linking (meth)acryloyl group[2,4–8] and epoxy group,[9,10] and amphiphilic architecture.[11–14]

Controlled polymerization techniques have been adopted to prepare well-defined polymers with controlled molecular weight, polydispersities, and terminal functionalities.[2,4,15–17] Living polymerizations have been achieved via ROMP catalyzed by the Grubbs catalyst (I).[18,19] The norbornene derivatives containing carbazoyl, phthalimide, epoxy group and *exo*-isomer were synthesized and their homopolymers were also prepare via living ROMP with I. Of particular interest is a combination of two of these processes for the formation of new polymeric materials.[2,4,6,17,20] The combination of ring-opening metathesis polymerization (ROMP) and atom radical transfer polymerization (ATRP) was employed to prepare some organosoluble polymeric materials.[15,16]



I

Cy = cyclohexyl
Ph = phenyl

Cross-linkable polymers have found a wide demand in the domain of nonlinear optical materials, interpenetrating polymer

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networks, macro- and microlithography, and more chemically and thermally resistant materials.[21] The development of polymers with cross-linkable end groups such as (meth)acryloyl group is one of interest for the preparation of AB cross-linked polymeric materials, interpenetrating polymer network, and for the immobilization of biomaterials.[1,2,4,6]

Synthesis of amphiphilic polymer containing ionic pendant groups has been the goal of academic for the past years.[22–24] Of particular interest is a class of amphiphilic polymer that undergo spontaneous self-organization in media mainly due to the hydrophobic associations to form various types of micelle-like nanostructures.[25,26]

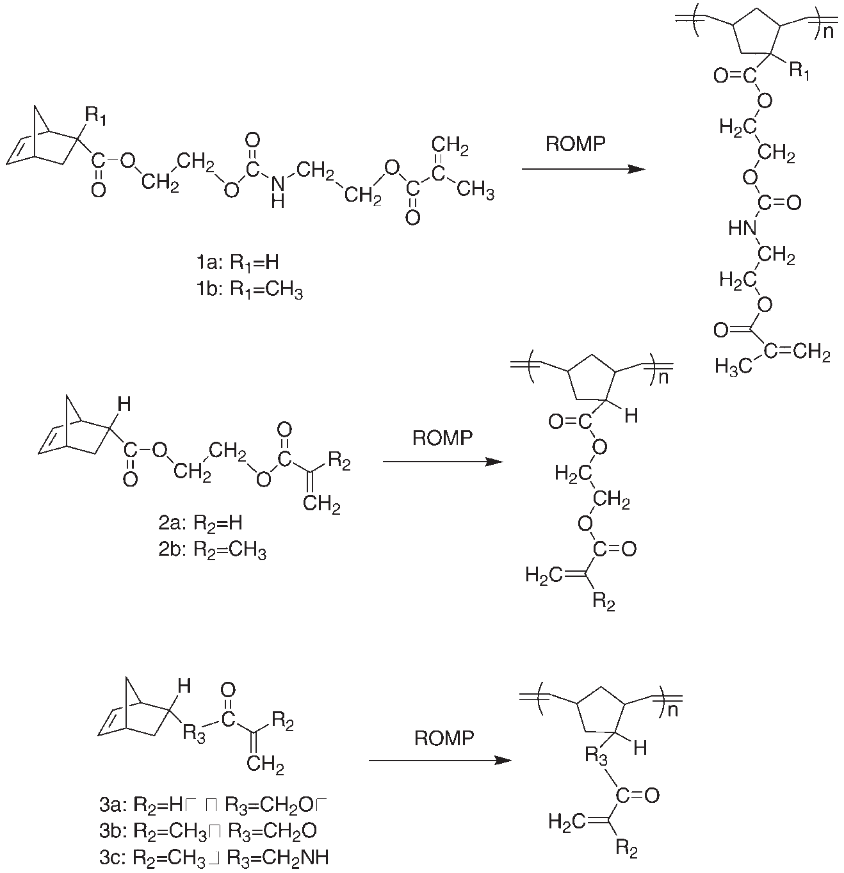
In this study, a series of functional norbornene derivatives with crosslinkable side chain such as (meth)acryloyl group, epoxy group, and with amphiphilic architecture for self assembling were introduced. Monomers used for combination of controlled polymerization techniques such as ROMP and ATRP were also described.

Crosslinkable Polynorbornenes via Ring-Opening Metathesis Polymerization

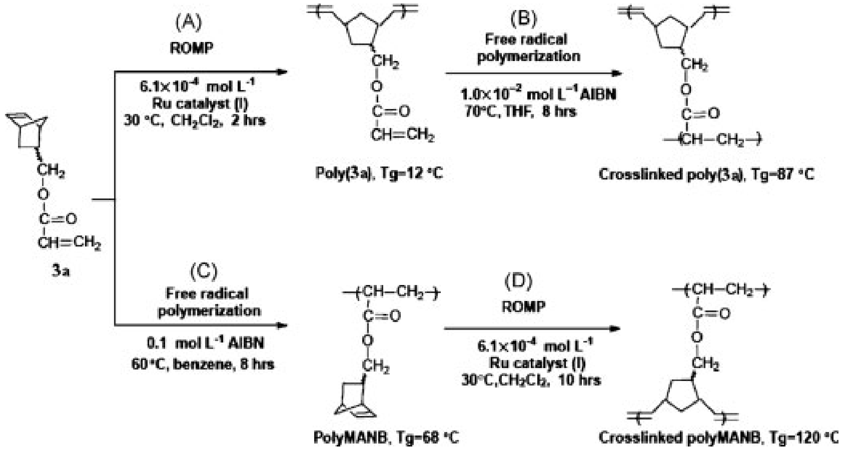
Crosslinkable polymers could be applied to nonlinear optical materials,[27] macro- and microlithography,[28] and interpenetrating polymer networks.[29] The (meth)acryloyl group and the epoxide group are widely employed as crosslinkable side chains within polymers. Polymers carrying pendent epoxide groups have been widely used in protective coatings, structural applications such as laminates and composites, molding, adhesives, and elsewhere. The development of polymers with crosslinkable methacryloyl groups is one of interest for the preparation of interpenetrating polymer networks, AB crosslinked polymeric materials, and for the immobilization of biomaterials.[1,19]

A serious of norbornene derives with pendant α,β-unsaturaturated amide or ester bridged chains were synthesized in our laboratory.[30] 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 1a,b (Scheme 1) showed excellent solubility. Organo-insoluble precipitate was obtained after ROMP of 3c with the amide group. It is possible to carry out ring-opening metathesis polymerization and conventional free radical polymerization of 3a as it contains a norbornene group and an acryloyl group. A novel organo-insoluble functional polynorbornene could be obtained after ROMP of 3a (Scheme 2(A)). The resulting functional polynorbornene, poly(3a), still contains cross-linkable side chains and shows a glass transition temperature (T_g) value of 12 °C. Furthermore, poly(3a) was cross-linked by thermal free radical polymerization (Scheme 2(B)). Glass transition temperature (T_g) of the resulting cross-linked poly(3a) was observed at 87 °C. Also, an intended polymer with norbornene side chains [poly(MANB)] has been prepared (Scheme 2(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 2(D)). A series of functional norbornenes were prepared. Organoinsoluble 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 I because the ethylene between the urethane group and ester group of poly(3a,b) enhanced solubility. High performance polynorbornenes with crosslinkable groups could be designed with high potential for practical application.

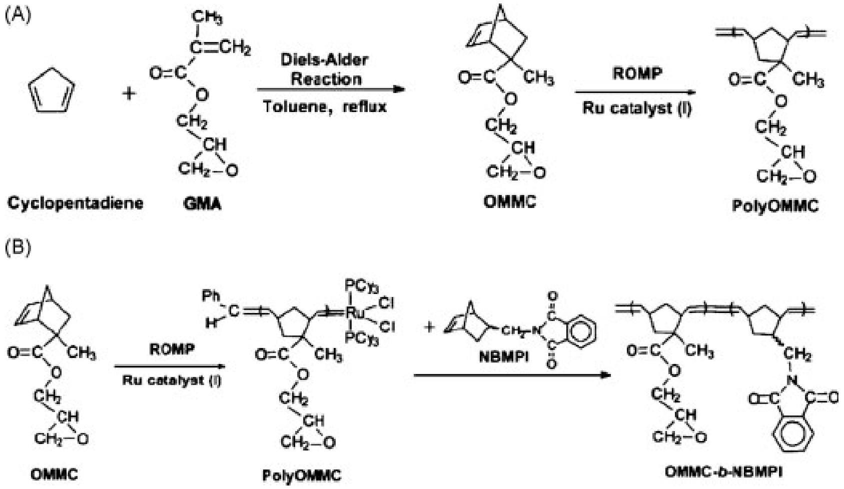
A new functional norbornene monomer containing an epoxy group, OMMC, was synthesized by the Diels–Alder reaction of freshly cracked dicyclopentadiene and GMA. (Scheme 3) The ratio of OMMC endo- and exo-isomers was calculated to be 2/1 by NMR.[31] Polymerization of OMMC was carried out via ROMP using Ru



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



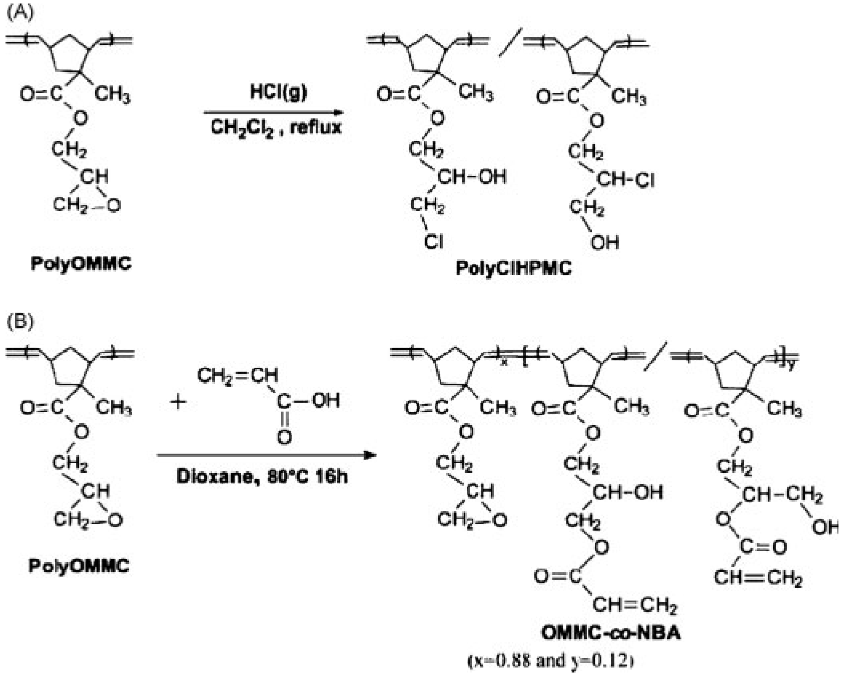
Scheme 2.
Cascades of ROMP and radical polymerization.



Scheme 3.
Synthesis of polynorbornene bearing active epoxy group: (A) polyOMMC and (B) diblock copolymer OMMC-b-NBMPI.

catalyst (I). Mn of polyOMMC linearly increased with the [monomer]/[catalyst] ratio and a narrow polydispersity was observed; this was considered a living polymerization (Scheme 3(A)). Therefore, a diblock polymerization was carried out using NBMPI as the second monomer (Scheme 3(B)).

As shown in Scheme 4, after modification with $HCl_{(g)}$ and acrylic acid, chloro-



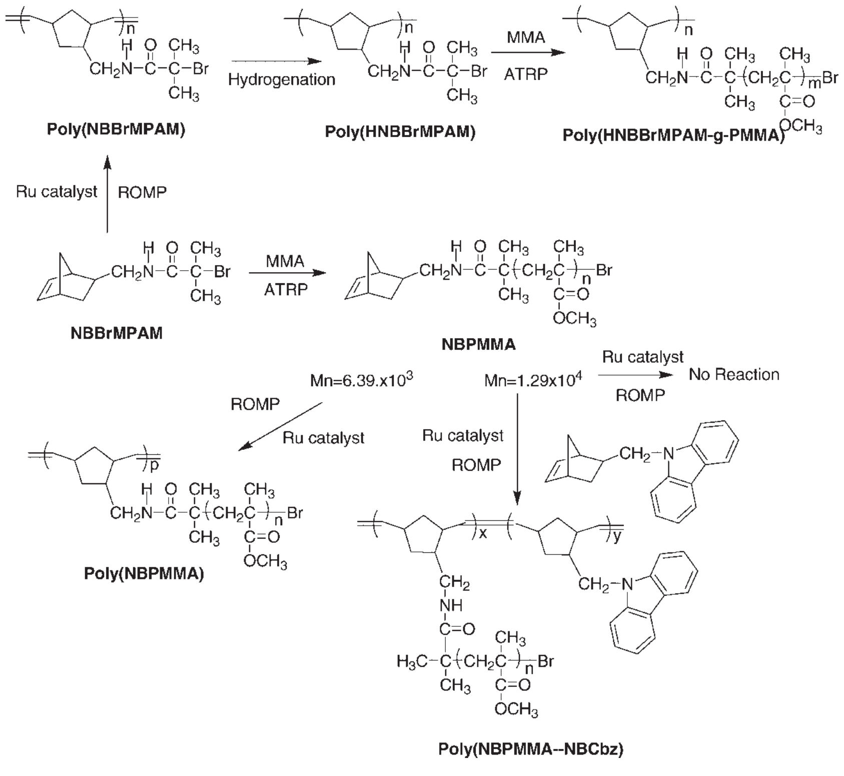
Scheme 4.
Modification of a polynorbornene bearing active epoxy moieties.

containing polyClHPMC and acrylated random OMMC-co-NBA were obtained, respectively. Both modified polymers contained functional hydroxyl groups, which could be considered for use in further modification. The modification proceeded to give the corresponding polynorbornene carrying pendant functional chloromethyl groups, which could be further applied to be as a new macroinitiator for ATRP. High performance polynorbornene with active epoxy groups could be designed with great potential for applications in photoresists, UV curing, and elastomers.

Combination of Ring-Opening Metathesis Polymerization (ROMP) and Atom Transfer Radical Polymerization (ATRP)

Controlled polymerization techniques have been adopted to prepare well-defined polymers with controlled molecular weight, polydispersities, and terminal functionalities.[15,32–34] Of particular interest today is a combination of two of these processes for the formulation of ner polymer materials. We had polymerized new materials via a combination of ROMP and ATRP (Scheme 5).[35]

A novel active norbornene derivative [5-(2-bromo-2-methylpropionylaminomethyl) bicycle[2.2.1]hept-2-ene (NBBrMPAM)] was synthesized and the structure was confirmed. Poly(NBBrMPAM) was polymerized via ring-opening metathesis polymerization from NBBrMPAM, which was carried out at room temperature by using Ru catalyst (I). The average number molecular weights (Mn) of poly(NBBrMPAM) depended on [Monomer]/[catalyst] ratio. Graft copolymerization of poly(NBBrMPAM) and/or poly(HNBBrMPAM) macroinitiators with methyl methacrylate (MMA) was carried out and gel formation was observed during the ATRP even the molecular



Scheme 5.
Preparations of polymers derived from combination of ROMP and ATRP.

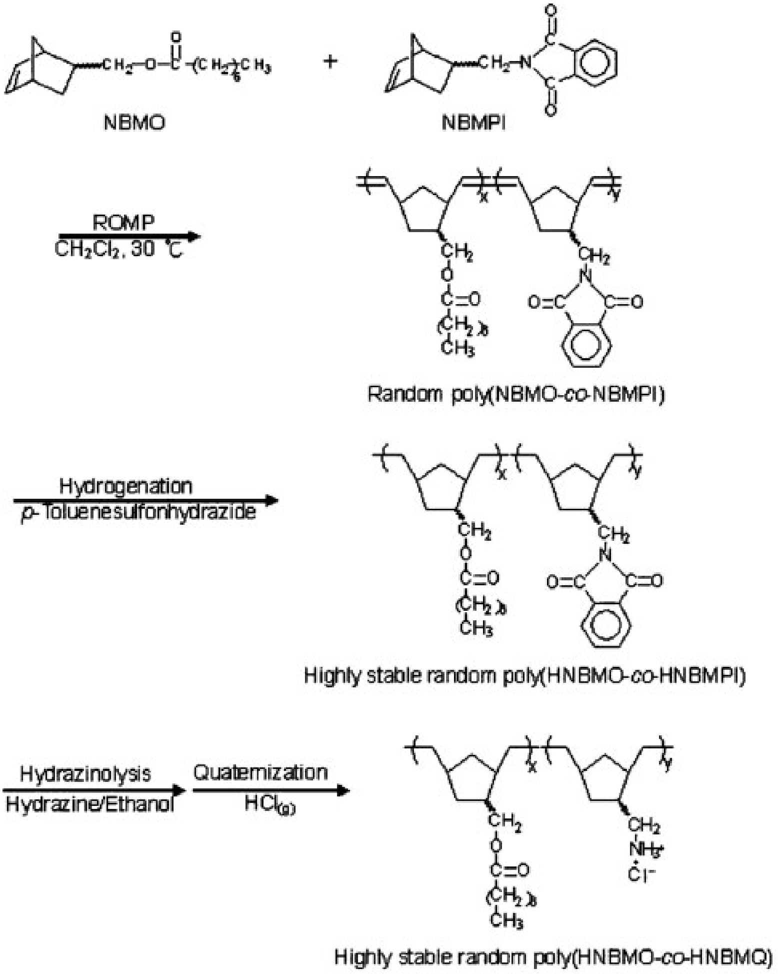
weight of macroinitiators smaller than 1.2×10^4 and reaction time shorter than 1 min. The graft copolymers were insoluble in common organic solvents and were presumed to be highly crosslinked because of crosslinking of the side chain.[36] One of the demerits of using ATRP to grow the side chains from the backbone is that radical-radicak coupling may lead to crosslinked polymers or polymers with multimodal molecular weight distributions. To avoid this, various conditions of the polymerization, including temperature, catalyst, and initiator concentrations, were optimized to prevent the termination by radical–radical coupling as much as possible during polymerization.[36] Also, the solvent plays an important role in the radical polymerization. Graft copolymerization of poly(HNBBrMPAM) with MMA was carried out in diluted macroinitiator solution ([poly(HNBBrMPAM)]=3.64×10^{-2} mole $\cdot$ L^{-1} in THF at 65 °C) to afford graft poly (HNBBrMPAM-g- PMMA). Graft poly(HNBBrMPAM-g-PMMA) was obtained with a monomodal molecular weight distribution within 15 min (Mn = 2.67×10^4). After 15 min, graft products were insoluble and trace soluble products were isolated from the insoluble part, which is due to radical–radical coupling during polymerization. The trace soluble product [poly (HNBBrMPAM-g-PMMA)] with bimodal molecular weight distribution was observed.

Polymethyl methacrylate macromonomer with end-capping norbornenyl group (NBPMMA) is derived from NBBrMPAM via ATRP. There are some problems in the preparation of poly(macromonomer) because of the molecular weight of macromonomer. Homopolymer poly(NBPMMA) could be obtained by controlling monomer concentration and reaction time (5 min) from macromonomer NBPMMA with lower molecular weight (6.39×10^3) via ROMP, but could not be obtained from macromonomer NBPMMA with higher molecular weight (1.29×10^4). However, copolymerization of NBPMMA macromonomer (Mn $> 1.0 \times 10^4$) with a low molecular weight comonomer was carried out for the synthesis of branched copolymer by ROMP. Carbazole-containing norbornene derivative (NBCbz) was employed as a comonomer to prepare poly(norbornene methylene carbazoleco-α-norbornenyl polymethyl methacrylate macromonomer),poly(NBPMMA-co-NBCbz), by ROMP with Ru catalyst (I). Fluorescence spectrum of poly(NBPMMA-co-NBCbz) exhibited a strong carbazole fluorescence emission due to carbazole moiety. This is the first ever attempt to prepare novel organosoluble fluorescent materials by using highly stable saturated macroinitiators via the combination of ROMP and ATRP.

Self-Assembly Aggregation of Copolynorbornenes via ROMP

Synthesis of amphiphilic polymers containing ionic pendant groups has been the goal of academic for the past years. Recently, amphiphilic polymers undergo spontaneous self-organization in media mainly due to the hydrophobic associations to form various types of micelle-like nanostructures.[25] Novel stable copolynorbornenes with self-assembly amphiphilic architecture containing hydrophilic ammonium salt and hydrophobic alkyl ester group were obtained by ring-opening metathesis polymerization, hydrogenation, hydrazinolysis, and subsequent quaternization.[5] The preparation of copolynorbornens derived from NBMO and NBMPI is shown in Scheme 6.

In various polymerization experiments, the ratio of $[M]_{NBMO}$/[Catalyst] was maintained 250 and the $[M]_{NBMPI}$/[Catalyst] was raised from 250 to 1000. Random poly(NBMO-co-NBMPI)s exhibited unimodal molecular weight distribution curves. Mn increased with the increase of $[M]_{NBMPI}$/[Catalyst]. When the content of NBMPI increased from 50 to 80 mol% in the random copolymerization system, the nature of GPC curve becomes a broad molecular weight distribution with a shoulder. It might be due to the difference in the reactivity of propagation polymer metallacarbene toward living monomer, NBMPI,[37] and non-living monomer, NBMO. After hydrogenation of poly(NBMO-co-NBMPI)s, the hydrazinolysis



For random poly(HNBMO-*co*-HNBMQ)-1, x/y = 250/250, $f_{HNBMQ(th)}$ = 50 mol%, $f_{HNBMQ(exp)}$ = 48.7 mol%
For random poly(HNBMO-*co*-HNBMQ)-2, x/y = 250/500, $f_{HNBMQ(th)}$ = 67 mol%, $f_{HNBMQ(exp)}$ = 67.2 mol%
For random poly(HNBMO-*co*-HNBMQ)-3, x/y = 250/750, $f_{HNBMQ(th)}$ = 75 mol%, $f_{HNBMQ(exp)}$ = 74.9 mol%

Scheme 6.
Preparation of Highly Stable Random Poly(HNBMO-co-HNBMQ).

was carried out by using hydrazine monohydrate, and then the quaternized random copolynorbornenes containing hydrophilic ammonium salt were obtained by the reaction with $HCl_{(g)}$. (Scheme 6) It is interesting to find the individual micelles of random copolymers with composition range from 50 to 75 mol% ammonium salt (f_{HNBMQ}) in SEM and TEM micrographs as isolated nanomer-scale spherical, and their average diameters were in the range of 6.8–18.1 nm in SEM and 5.0–13.7 nm in TEM micrographs. The SEM results indicate that the intrapolymer aggregates formed by the random copolymer might be due to the formation of unimer (Figure 1A) depending on the molar ratio of hydrophobic/hydrophilic group. When ammonium salt content (f_{HNBMQ}) was increased more than 80 mol %

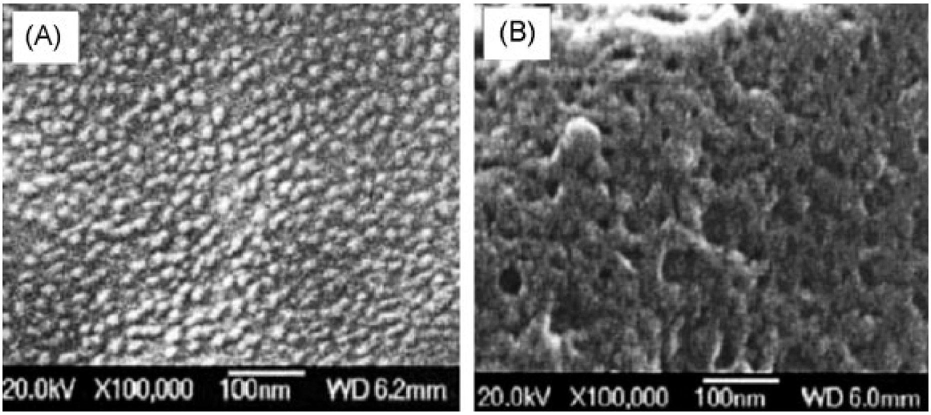


Figure 1.
SEM micrographs of random poly(NBMO-co-NBMPI) (A) $f_{HNBMQ} = 75$ mol %, and (B) $f_{HNBMQ} = 80$ mol %. Both were prepared in ethanol/methylene chloride (2/1, v/v).

($f_{HNBMQ(exp)} = 76.6$ mol% by ^{1}H NMR), the micelle morphology changed from spherical to network-like aggregates (Figure 1B) which is due to hydrophobically crosslinked chains of interpolymers.

Conclusion

Some ring-opening metathesis polymerization (ROMP) of norbornene derivatives containing functional groups has been introduced. Controlled polymerization characterization of ROMP is adapted to prepare well-defined polymers with controlled molecular weights, narrow polydispersities, and terminal functionalities. Combination with other polymerization techniques such as free radical polymerization and ATRP, unique molecular architecture can be designed for further applications.

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