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Notes

Self-Assembly Aggregation of Highly Stable Copolynorbornenes with Amphiphilic Architecture via Ring-Opening Metathesis Polymerization

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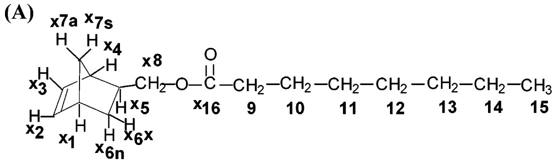
Introduction

Synthesis of amphiphilic polymer containing ionic pendant groups has been the goal of academic for the past several years.[1–6] Many researchers have focused on fluorescent-labeled amphiphilic polymers to correlate the microscopic, photophysical response with a macroscopic event such as self-association, phase separation, aggregation, or latex film formation.[7–12] Of particular interest is a class of amphiphilic polymers that undergo spontaneous self-organization in media mainly due to the hydrophobic associations to form various types of micelle-like nanostructures.[12,13] Since the commercial introduction of cyclic olefin copolymers (COCs) such as Zeon's Zeonex and Zeonor and Ticona's Topas products, there has been increasing interest in high-performance hydrocarbon polymers obtained via ring-opening metathesis polymerization (ROMP) and hydrogenation, the method of choice for producing completely amorphous COCs. The chemical and electronic properties of these polymers make them potentially useful as photoresists.[14–19]

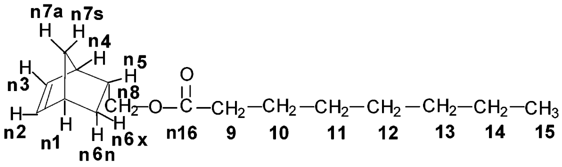
In this investigation, novel stable copolynorbornenes with self-assembly amphiphilic architecture containing hydrophilic ammonium salt and hydrophobic alkyl ester group were obtained by ring-opening metathesis polymerization (ROMP), hydrogenation, hydrazinolysis, and subsequent quaternization. Various random copolymers with varying compositions of bicyclo[2.2.1]hept-5-en-2-ylmethyl octanoate (NBMO) and 5-(phthalimide methyl)-bicyclo[2.2.1]hept-2-ene (NBMPI) were synthesized to control the interaction and microstructure of aggregates via ROMP. The formation, structure, and morphologies of the aggregates will be investigated. The association of polymer molecules in water will be confirmed by fluorescence spectroscopy. The size and morphologies of aggregates will be characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Experimental Section

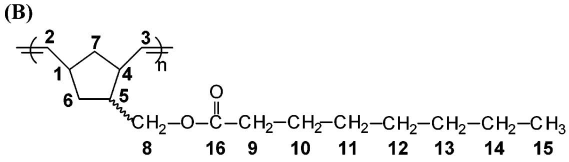
Scheme 1. Structures of (A) NBMO Isomer and (B) Poly(NBMO)



exo-isomer (NBMO)



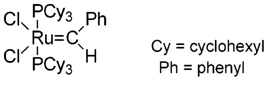
endo-isomer (NBMO)



Poly(NBMO)

Synthesis of Bicyclo[2.2.1]hept-5-en-2-ylmethyl Octanoate (NBMO). The alkyl ester derivative of norbornene such as bicyclo[2.2.1]hept-5-en-2-ylmethyl octanoate (NBMO) was prepared as described with previous literature.[20–22] The yield of NBMO was 83% (bp = 134 °C/4 mmHg, *endo*/*exo* = 82/18). The ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.54–0.57 (H_{n6n}; 1H), 0.87–0.92 (H_{15}; 3H), 1.14–1.18 (H_{x6n}; 1H), 1.24–1.31 (H_{x6x}, H_{n7a}, H_{x7a}, H_{x7s}, and H_{11-14}; 12H), 1.44–1.46 (H_{n7s}; 1H), 1.60–1.64 (H_{10}; 2H), 1.69–1.75 (H_{x5}; 1H), 1.81–1.86 (H_{n6x}; 1H), 2.28–2.33 (H_9; 2H), 2.35–2.42 (H_{n5}; 1H), 2.69 (H_{x1}; 1H), 2.81–2.83 (H_{n1} and H_{x4}; 2H), 2.87 (H_{n4}; 1H), 3.63–3.87 (H_{n8}; 2H), 3.94–4.16 (H_{x8}; 2H), 5.92–5.94 (H_{n3}; 1H), 6.06–6.10 (H_{x2}, and H_{x3}; 2H), and 6.14–6.16 (H_{n2}; 1H). The ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 14.08 (C_{15}), 22.64 (C_{14}), 25.12 (C_{13}), 28.98 (C_{12}), 29.03 (C_{n6}), 29.17 (C_{11}), 29.63 (C_{x6}), 31.72 (C_{10}), 34.42 (C_9), 37.90 (C_{n5}), 38.06 (C_{x5}), 41.64 (C_{x1}), 42.25 (C_{n1}), 43.72 (C_{x4}), 43.92 (C_{n4}), 44.99 (C_{x7}), 49.40 (C_{n7}), 67.64 (C_{n8}), 68.33 (C_{x8}), 132.20 (C_{n3}), 136.24 (C_{x3}), 136.90 (C_{x2}), 137.53 (C_{n2}), 173.75 (C_{n16}), and 173.84 (C_{x16}) (Scheme 1A). IR (cm^{-1}, KBr): 717 (C=C, olefinic), 1734 (C=O, asymmetric). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.99; H, 10.68.

Ring-Opening Metathesis Polymerization of NBMO. A solution of catalyst was prepared by dissolving metathesis catalyst **1** (3 mg, 3.6 × 10^{-3} mmol) in 1 mL of anhydrous methylene chloride in an argon-filled drybox. The monomer NBMO (0.2 g, 0.8 mmol) was dissolved in 10 mL of methylene chloride and then degassed via a freeze–pump–thaw cycle. After degassing the monomer solution completely, the catalyst solution was injected into the monomer solution by a syringe.



$$Cl_2(PCy_3)_2Ru{=}CHPh$$

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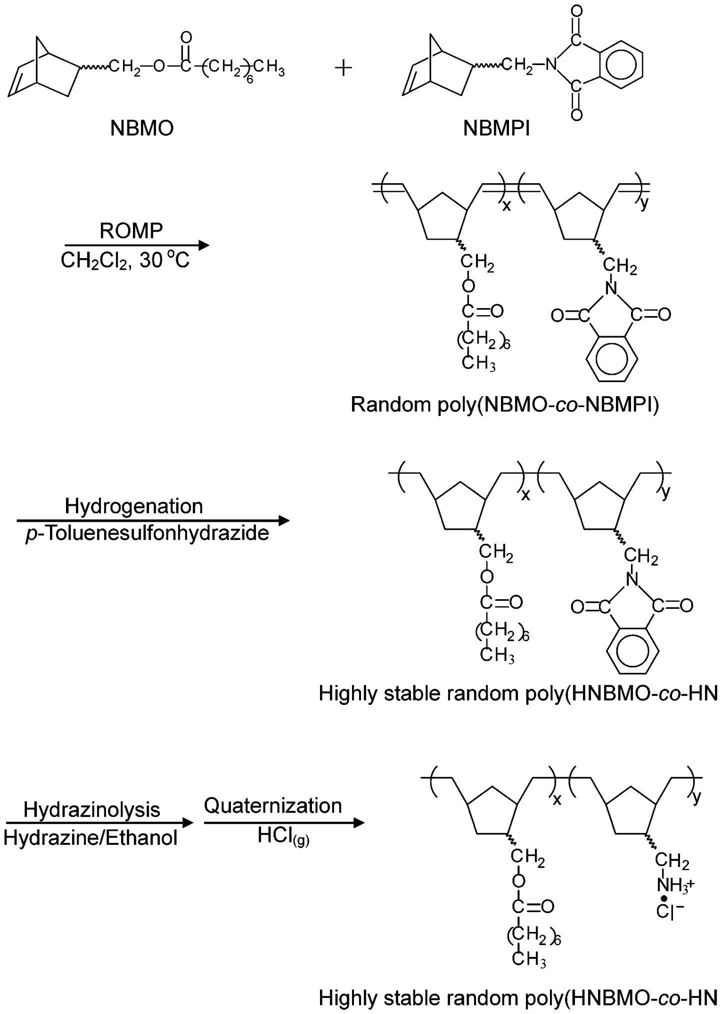
Scheme 2. Preparation of Highly Stable Random Poly(HNBMO-*co*-HNBMQ)



For random poly(HNBMO-*co*-HNBMQ)-1, x/y = 250/250, $f_{\mathrm{HNBMQ(th)}}$ = 50 mol%, $f_{\mathrm{HNBMQ(exp)}}$ = 48.7 mol%
For random poly(HNBMO-*co*-HNBMQ)-2, x/y = 250/500, $f_{\mathrm{HNBMQ(th)}}$ = 67 mol%, $f_{\mathrm{HNBMQ(exp)}}$ = 67.2 mol%
For random poly(HNBMO-*co*-HNBMQ)-3, x/y = 250/750, $f_{\mathrm{HNBMQ(th)}}$ = 75 mol%, $f_{\mathrm{HNBMQ(exp)}}$ = 74.9 mol%
For random poly(HNBMO-*co*-HNBMQ)-4, x/y = 250/1000, $f_{\mathrm{HNBMQ(th)}}$ = 80 mol%, $f_{\mathrm{HNBMQ(exp)}}$ = 76.6 mol%

The polymerization was carried out at 30 °C for 2 h. The reaction was terminated by the addition of a small amount of ethyl vinyl ether (0.2 mL) and polymer; poly(NBMO) was obtained by precipitating in excess methanol and further purified by dissolving in methylene chloride and reprecipitating in methanol. Polymer was dissolved in benzene, filtered, frozen, and dried. The yield of the poly(NBMO) was 90%. IR (cm^{-1}, KBr): 970 (C=C, olefinic), 1732 (C=O, asymmetric). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.86−0.89 (H_{15}; 3H), 1.20−3.00 (H_1, H_4, H_5, H_6, H_7, and H_{9-14}; 19H), 3.87−4.03 (H_8; 2H), and 5.21−5.33 (H_2 and H_3; 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 14.09 (C_{15}), 22.61 (C_{14}), 25.02 (C_{13}), 28.96 (C_{12}), 29.16 (C_{11}), 31.69 (C_{10}), 34.45 (C_9), 35.82−46.55 (C_1, C_4, C_5, C_6, and C_7), 66.08−66.97 (C_8), 129.47−134.86 (C_2 and C_3), and 173.89 (C_{16}) (Scheme 1B).

Hydrogenation of Poly(NBMO). The polymer poly(NBMO) (0.30 g, 1.2 mmol) was dissolved in 20 mL of xylene in a Schlenk tube. To the above solution, 1.64 g (8.8 mmol) of hydrogenating agent, *p*-toluenesulfonhydrazide (7.3 equiv relative to the repeating unit), and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) were added. The polymer solution with hydrogenating agent was then degassed thrice via a freeze−pump−thaw cycle and sealed. The solution was stirred at 120 °C for 12 h until the evolution of nitrogen stopped. The hydrogenated polymer poly(HNBMO) was obtained by precipitating in excess methanol and further purified by dissolving in methylene chloride and reprecipitating in methanol. Polymer was dissolved in benzene, filtered, frozen, and dried. The yield of poly(HNBMO) was 87%.

Preparation of Random Poly(NBMO-*co*-NBMPI) via Ring-Opening Metathesis Polymerization. The monomer NBMPI was prepared by azeotropic removal of water from an equimolar solution of 5-(aminomethyl)bicyclo[2.2.1]hept-2-ene (NBMA) and phthalic anhydride in xylene as previously reported; mp = 99−100 °C.[23] The random copolymer of NBMO and NBMPI was obtained by ROMP using catalyst **1**, as outlined in Scheme 2. The yield of random poly(NBMO-*co*-NBMPI) was about 92%. The molar fractions of copolymers were estimated from the relative peak area of phthalic aromatic proton resonance and olefinic proton resonance.

Hydrogenation, Hydrazinolysis, and Quaternization of Random Poly(NBMO-*co*-NBMPI). Hydrogenation of random poly(NBMO-*co*-NBMPI) was carried out by using *p*-toluenesulfonhydrazide as hydrogenating agent, described in the previous reaction. The yield of the hydrogenated copolymer, random poly(HNBMO-*co*-HNBMPI), was 87%.

Random poly(HNBMO-*co*-HNBMPI) (0.2 g, 0.8 mmol) was suspended in 15 mL of ethanol in a Schlenk tube. To the above mixture, 5 mL of hydrazine monohydrate was added. The mixture was degassed thrice via a freeze−pump−thaw cycle, and then the tube was heated to 100 °C. Hydrazinolysis was continued for 12 h. The quaternization was subsequently

Table 1. Effect of [Monomer]/[Catalyst] Ratio ([M]/[C]) on Polymer Yield and Molecular Weight in Homopolymerization of NBMO and Its Random Copolymerization with NBMPI by Ring-Opening Metathesis Polymerization

polymer code	$[M]_{NBMO}/[C]^a$	$[M]_{NBMPI}/[C]^b$	yield (%)	$M_n \times 10^5$ (calcd)	$M_n \times 10^{5\,c}$	PDI^d
poly(NBMO)	250		85	0.63	0.48	1.4
poly(NBMO)	500		88	1.27	0.96	1.7
poly(NBMO)	750		90	1.90	1.12	1.9
poly(NBMO)	1000		94	2.53	1.74	2.0
random poly(NBMO-*co*-NBMPI)-1	250	250	86	1.26	0.83	1.5
random poly(NBMO-*co*-NBMPI)-2	250	500	92	1.89	1.42	2.9^e
random poly(NBMO-*co*-NBMPI)-3	250	750	94	2.52	1.98	4.9^e
random poly(NBMO-*co*-NBMPI)-4	250	1000	94	3.16	2.17	6.1^e

[a] $[M]_{NBMO}$: molar concentration of bicyclo[2.2.1]hept-5-en-2-ylmethyl octanoate; [C]: molar concentration of the catalyst. [b] $[M]_{NBMPI}$: molar concentration of 5-(phthalimide methyl)bicyclo[2.2.1]hept-2-ene; [C]: molar concentration of the catalyst. [c] As determined by GPC in THF using polystyrene as a calibration standard. [d] PDI: polydispersity index. [e] Due to a broad molecular weight distribution with a shoulder.

carried out by using $HCl_{(g)}$ at room temperature for 2 h. The quaternized copolymer was dissolved in water, filtered, and then precipitated from acetone. The yield of the quaternized copolymer, random poly(HNBMO-*co*-HNBMQ), was 75%. Random poly(HNBMO-*co*-HNBMQ)s with the molar fraction of HNBMQ segment feed in the experiment ($f_{HNBMQ(th)}$) = 50−80 mol % ($f_{HNBMQ(exp)}$ = 48.7−76.6 mol %) were obtained.

Results and Discussion

Characterization of Bicyclo[2.2.1]hept-5-en-2-ylmethyl Octanoate (NBMO). The structure of NBMO was characterized by the ^{1}H NMR, ^{13}C NMR, H−H COSY, and H−C COSY spectra. The ratio of *endo*- and *exo*-isomer was calculated to be 82/18 from the intensity of signals of olefinic hydrogens H_{n8} and H_{x8} (Scheme 1A). A stronger coupling between the two protons H_{n5} and H_{n6x} of the *endo*-isomer than the H_{x5} and H_{x6n} of the *exo*-isomer was observed despite identical dihedral angles.[24] The signals of protons (H_{n5}) and its coupling partner (H_{n6x}) with high coupling constant were identified and assigned as signals of the *endo*-isomer.[24] Likewise, the signals of protons (H_{x5}) and its coupling partner (H_{x6n}) with lower coupling constant were identified from H−H COSY spectrum and assigned as signals of the *exo*-isomer.[24] Once these well-defined couplings were located, the rest of the protons could be identified on the basis of the H−H and H−C COSY spectra. Upon identification of chemical shifts of the individual isomer using H−H COSY connectivities, it was observed that monomer NBMO was synthesized with preferential formation of *endo*-isomer (82%).

Characterization of Poly(NBMO) and Poly(HNBMO). Ring-opening metathesis polymerization of NBMO was carried out by using catalyst **1**, and the ratio of molar concentration of monomer $[M]_{NBMO}$ to catalyst [C] was varied from 250 to 1000. The yield of polymer, number-average molecular weight (M_n), and polydispersity index (PDI) data are summarized in Table 1. From Table 1, it can be seen that M_n increased with the increase of $[M]_{NBMO}/[C]$, and PDI values were in the range of 1.4 and 2.0.

The proton signals of olefinic hydrogens of norbornene ring at δ (ppm) 5.92 and 6.16 disappeared. In the ^{1}H NMR spectrum of poly(NBMO), it showed new broad olefinic signals between δ (ppm) 5.21 and 5.33. It allows us to calculate ratio of *trans* and *cis* content from ^{1}H NMR and estimate to be 86/14 for poly(NBMO). In the ^{13}C NMR spectrum, the signals at δ (ppm) 35.82−46.55 were assigned to the carbons of cyclic structure of the poly(NBMO), and various olefinic carbons of the ring-opened polymer backbone resonance signals appeared between δ (ppm) 129.47 and 134.86. Poly(NBMO) was highly soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, methylene chloride, and benzene but partially soluble in dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF). The poly(NBMO) with $M_n = 1.12 \times 10^5$ ($[M]_{NBMO}/[C] = 750$) showed the glass transition temperature (T_g) at −37 °C, and 10% decomposition temperature ($T_d^{10\%}$) was observed at 393 and 385 °C in the atmosphere of nitrogen and air, respectively. The weight loss of 90−100% for all samples was observed over 600 °C. In each of the analyses, single step weight loss were observed consistently. Saturation of the double bond for poly(NBMO) has led to an increase in 10% decomposition temperature of about 10 °C under nitrogen atmosphere ($T_d^{10\%}$ = 401 °C).

Chacterization of Various Random Copolymers [Random Poly(NBMO-*co*-NBMPI)]. In various polymerization experiments, the ratio of $[M]_{NBMO}/[C]$ was maintained constant (250), and the $[M]_{NBMPI}/[C]$ was raised from 250 to 1000. Random poly(NBMO-*co*-NBMPI)s exhibited unimodal molecular weight distribution curves. From Table 1, M_n increased with the increase of $[M]_{NBMPI}/[C]$. 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 propagating polymer metallacarbene toward living monomer, NBMPI,[23] and nonliving monomer, NBMO. The ^{1}H NMR spectrum of random poly(NBMO-*co*-NBMPI)-3 showed new broad signals due to olefinic protons between δ (ppm) 5.29 and 5.45 (Figure 1A). In the ^{13}C NMR spectrum, the signals at δ (ppm) 36.68−44.09 are ascribed to the carbons in the cyclic structure of random poly(NBMO-*co*-NBMPI)-3. The resonance signals of olefinic carbons of the polymer main chain appeared between δ (ppm) 128.27 and 135.07. The molar fraction of random poly(NBMO-*co*-NBMPI) was estimated from the relative peak area of phthalic aromatic proton resonance and olefinic proton resonance. The molar fractions of NBMPI ($f_{NBMPI(exp)}$) for poly(NBMO-*co*-NBMPI)-1, -2, -3, and -4 were calculated to be 48.7, 67.2, 74.9, and 76.6 mol %, respectively. To obtain an organo-soluble amino-containing copolymer, the content of amino pendent group is limited to be 13.2 mol %. The molar fraction of NBMO ($f_{NBMO(exp)}$) for random poly(NBMO-*co*-NBMPI)-5 was estimated to be 86.8 mol % from the relative peak area of methyl proton resonance and olefinic proton resonance. After hydrazinolysis of poly(NBMO-*co*-NBMPI)-5, an organo-soluble poly(NBMO-*co*-NBMA)-5 with 13.2 mol % amino-containing segment was obtained. The content of alkyl ester group ($f_{NBMO(exp)}$ = 86.8 mol %) was still remained in the poly-

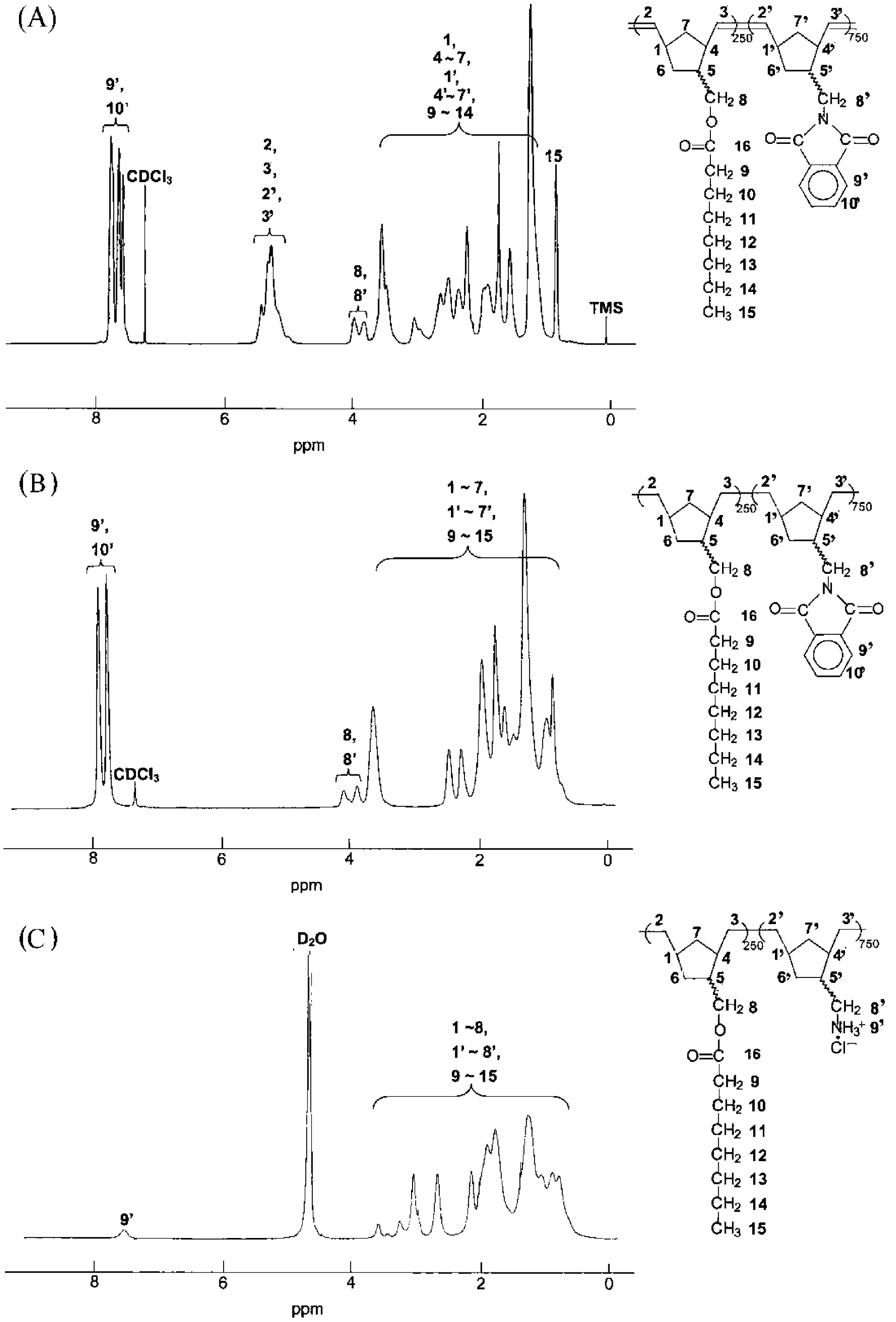


Figure 1. ^{1}H NMR (500 MHz) spectra of (A) random poly(NBMO-*co*-NBMPI)-3, (B) random poly(HNBMO-*co*-HNBMPI)-3, and (C) random poly(HNBMO-*co*-HNBMQ)-3.

(NBMO-*co*-NBMA)-5 after hydrainolysis of poly(NBMO-*co*-NBMPI) ($f_{\mathrm{NBMO(exp)}}$ = 86.8 mol %) and confirmed by the ^{1}H NMR and ^{13}C NMR spectra (Figure 2). In the ^{1}H NMR and ^{13}C NMR spectra of random poly(NBMO-*co*-NBMA)-5, the signals due to protons of alkyl ester (H_9-H_{15} in Figure 2) at δ (ppm) 0.87 (H_{15}), 1.28 ($H_{11}-H_{14}$), 1.59 (H_{10}), and 2.26 (H_9) and the signals due to carbons of alkyl ester (C_9-C_{16} in Figure 2) at δ (ppm) 36.80 (C_9), 34.45 (C_{10}), 29.14 (C_{11}), 28.94 (C_{12}), 25.01 (C_{13}), 22.59 (C_{14}), 14.07 (C_{15}), and 173.8 (C_{16}) were still remained.

The thermal stability of various polymers such as poly(NBMO) and random poly(NBMO-*co*-NBMPI) was compared. Better thermal stability of random poly(NBMO-*co*-NBMPI) having phthalimide groups was exhibited than poly(NBMO). Likewise, the influence of thermal stability on the hydrogenation was performed. For instance, the order of the temperatures at which 10% weight loss is poly(NBMO) (393 °C) < poly(HNBMO) (401 °C) < random poly(NBMO-*co*-NBMPI) (410 °C) < random poly(HNBMO-*co*-HNBMPI) (426 °C). Rapid weight loss of poly(NBMO-*co*-NBMPI)s does not occur until >400 °C under nitrogen, and all copolymers were decomposed in a single step. Random poly(NBMO-*co*-NBMPI)s similarly have one T_g value at about 35 °C, which is quite different from poly(NBMO) (T_g = −37 °C) and poly(NBMPI) (T_g = 144 °C).

After hydrogenation, the resonance signals of olefinic protons in the ^{1}H NMR spectrum of reactant between δ (ppm) 5.29 and 5.45 disappeared completely (Figure 1B). The aromatic resonance signals of the hydrogenated random copolymer between δ (ppm) 7.60 and 7.78

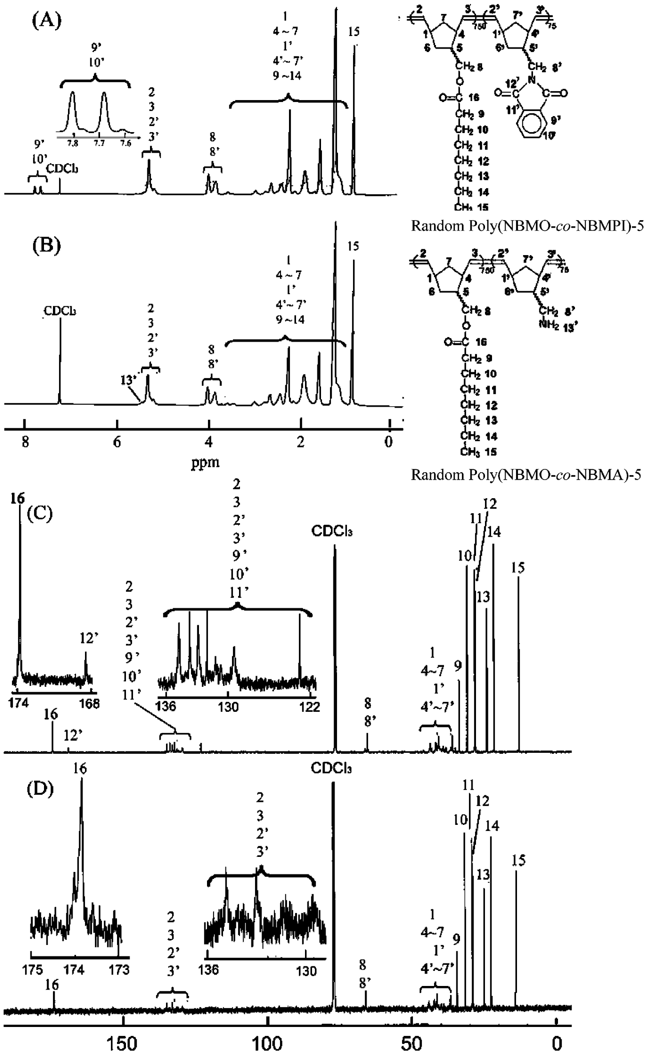


Figure 2. ^{1}H NMR (500 MHz) spectra of (A) random poly(NBMO-*co*-NBMPI)-5 and (B) random poly(NBMO-*co*-NBMA)-5; ^{13}C NMR (125 MHz) spectra of (C) random poly(NBMO-*co*-NBMPI)-5 and (D) random poly(NBMO-*co*-NBMA)-5.

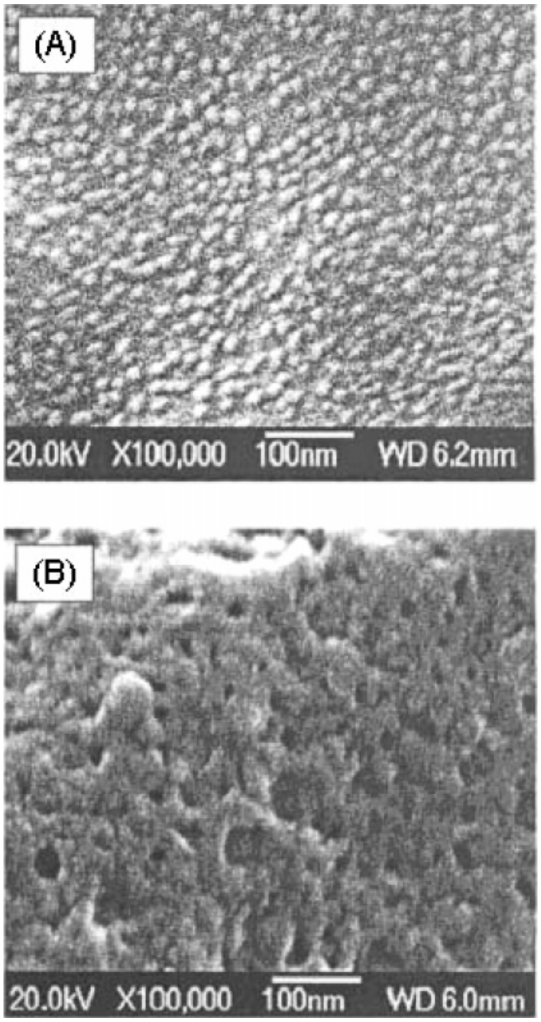


Figure 3. SEM micrographs of (A) random poly(HNBMO-*co*-HNBMQ)-3, $f_{\mathrm{HNBMQ}} = 75$ mol %, and (B) random poly(HNBMO-*co*-HNBMQ)-4, $f_{\mathrm{HNBMQ}} = 80$ mol %. Both were prepared in ethanol/methylene chloride (2/1, v/v).

still appeared which indicate the remaining phthalimide group. The hydrazinolysis of random poly(HNBMO-*co*-HNBMPI) was carried out by using hydrazine monohydrate, and then the quaternized random copolymer, random poly(HNBMO-*co*-HNBMQ)-3, was obtained by the reaction with $\mathrm{HCl}_{(g)}$ (Scheme 2). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ (ppm): 7.4−7.7 ($\mathrm{NH_3^+}$: 3H), due to hydrogens of quaternary ammonium ion (Figure 1C). Random poly(HNBMO-*co*-HNBMQ) with the molar fraction of HNBMQ segment feed in the experiment ($f_{\mathrm{HNBMQ(th)}}$) = 67−80 mol % ($f_{\mathrm{HNBMQ(exp)}}$ = 67.2−76.6 mol %) was soluble in water, methanol, and ethanol. The critical micelle concentrations (cmc) of random poly(HNBMO-*co*-HNBMQ)-2 ($f_{\mathrm{HNBMQ(th)}} = 67$ mol %; $f_{\mathrm{HNBMQ(exp)}} = 67.2$ mol % by ^{1}H NMR; Scheme 2) and random poly(HNBMO-*co*-HNBMQ)-3 ($f_{\mathrm{HNBMQ(th)}} = 75$ mol %; $f_{\mathrm{HNBMQ(exp)}} = 74.9$ mol % by ^{1}H NMR; Scheme 2) were observed at 0.1 and 0.3 g $\mathrm{dL^{-1}}$ in aqueous solution by fluorescence spectra.[12] Unfortunately, random poly(HNBMO-*co*-HNBMQ) with $f_{\mathrm{HNBMQ(th)}} = 50$ mol % ($f_{\mathrm{HNBMQ(exp)}} = 48.7$ mol % by ^{1}H NMR; Scheme 2) was soluble in ethanol and only partially soluble in water and methanol; hence, cmc could not be measured in aqueous solution. The cmc of poly(HNBMO-*co*-HNBMQ)-4 ($f_{\mathrm{HNBMQ(th)}} = 80$ mol %; $f_{\mathrm{HNBMQ(exp)}} = 76.6$ mol % by ^{1}H NMR; Scheme 2) could not be observed due to relatively high ammonium salt content and low surface activity.

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 nanometer-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. Nanometer-scale polymeric micelles having a uniform distribution of such random copolymers with 50−75 mol % of ammonium salts and 50−25 mol % of alkyl ester group were obtained. These results indicate that the intrapolymer aggregates formed by the random copolymer might be due to the formation of unimer (Figure 3A) depending on the molar ratio of hydrophobic group/hydrophilic group. When ammonium salt content (f_{HNBMQ}) was increased more than 80 mol % ($f_{\mathrm{HNBMQ(exp)}}$ = 76.6 mol % by ^{1}H NMR), the micelle morphology changed from spherical to network-like aggregates (Figure 3B) which is due to hydrophobically cross-linked chains of interpolymers.

Conclusions

Amphiphilic highly stable copolymers were successfully synthesized by ROMP, hydrogenation, hydrazinolysis, and quaternization. Nanometer-scale polymeric micelles having a uniform distribution of such random copolymers with 50−75 mol % of ammonium salts and 50−25 mol % of alkyl ester group were obtained, and their sizes were characterized by SEM (6.8−18.1 nm) and TEM (5.0−13.7 nm). As the content of hydrophilic ammonium salt in polymer reached to 80 mol %, the structure of random copolymer micelles changed to be network-like aggregates (hydrophobically cross-linked chains).

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