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Alternating Ring-Opening Metathesis Copolymerization of Amino Acid Derived Norbornene Monomers Carrying Nonprotected Carboxy and Amino Groups Based on Acid−Base Interaction

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Abstract: Amino acid derived norbornene monomers having carboxy (**1**) and amino groups (**2**) were synthesized and subjected to ring-opening metathesis copolymerization with various feed ratios using the Grubbs second generation ruthenium catalyst. The M_n's of the copolymers ranged from 5300 to 9400 ($M_w/M_n = 1.40-1.69$). The monomer conversion and M_n of the copolymer were maximized when the monomer feed ratio was 1:1. The monomer unit ratios in the copolymers were almost 1:1 at 10% conversion, irrespective of the feed ratios. The monomer reactivity ratios r_1 and r_2 were estimated to be 0.08 and 0.02, which confirmed that alternating copolymerization occurred. It is considered that alternating copolymerization is brought about by the acid−base interaction between the monomers and/or between the propagating polymer end and the incoming monomer.

Introduction

Precise control of polymer structure is an issue of great importance, not only in polymer chemistry but also in materials science, because of the improvement in properties of the resulting materials. Numerous studies have focused on the development of precisely controlled polymer synthesis. Ring-opening metathesis polymerization (ROMP) has attracted much attention due to the remarkable development of well-defined transition metal catalysts, including molybdenum and ruthenium (Ru) complexes.[1,2] In particular, ROMP of norbornene derivatives achieves a high level of control over tacticity, backbone configuration, molecular weight, and molecular weight distribution.[3−6] Among a wide variety of ROMP catalysts, Ru complexes developed by Grubbs and co-workers are highly tolerant toward polar functional groups under ambient conditions.[7] As a result, ROMP of functionalized norbornene derivatives facilitates the synthesis of functional polymers such as hydrogels,[8] biologically active polymers,[9−17] and liquid crystalline polymers.[18−20]

Copolymerization with controlled unit sequences is another approach to functionalize polymers. Living ROMP enables synthesis of block copolymers, some of which form micelles and nanoparticles,[21−30] which are applicable to emulsification, drug delivery control, sensing and patterning materials, and electroactive polymers. Thus, controlled ROMP raises interest, not only from the mechanistic aspect of polymer chemistry but also for the synthesis of functional materials. Alternating copolymerization is another method of synthesizing sequence-

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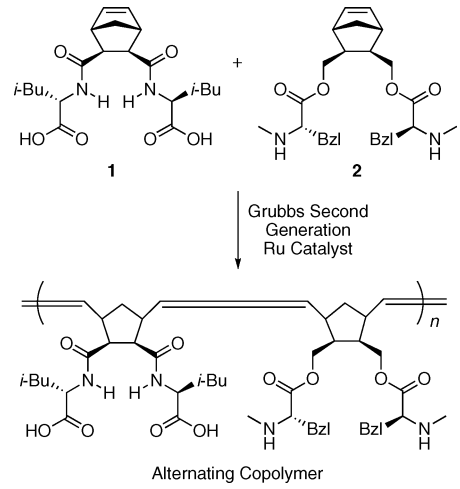
controlled copolymers.[31,32] This is commonly achieved by employing a combination of electron-accepting monomers like maleic anhydride with electron-donating monomers like alkyl vinyl ethers. In the case of ROMP, however, it is difficult to introduce electron-accepting or -withdrawing groups close to the double bond of cyclic olefin monomers. Therefore, other approaches have been used to attain alternating ring-opening metathesis copolymerization. For example, racemic 1-methylnorbornene undergoes ROMP alternatingly between the two enantiomeric monomers catalyzed with $ReCl_5$, but no homopolymerization takes place due to steric effects.[33] Alternating ring-opening metathesis copolymerization is also achieved by the combination of a small amount of highly polymerizable norbornene and a large amount of less polymerizable cyclopentene using $RuCl_3$-phenol[34] and Grubbs Ru complex-Lewis acid[35] as catalysts, wherein the "cage effect" plays an important role. Appropriately designed dual-site Ru carbene complexes catalyze the alternating copolymerization of norbornene and a large excess of cyclooctene, wherein one site of the complex shows chemoselectivity while the other site does not.[36,37] The combination of polar 2,3-difunctionalized 7-oxanorbornene derivatives and nonpolar cyclic olefins, including cyclooctene, also works satisfactorily.[38] The alternating copolymers form well-controlled micrometer-scale aggregates by complementary noncovalent interactions when diaminopyridine and thymine side chains are introduced. Very recently, cyclobutene 1-carboxylic esters and cyclohexene derivatives have been found to undergo alternating ring-opening metathesis copolymerization.[39] This success derives from the combination of two monomers, neither of which forms a homopolymer under ROMP conditions.

In spite of those attempts at alternating ring-opening metathesis copolymerization, to the best of our knowledge, there is no successful example of the combination of two kinds of norbornene monomers substituted with different functional groups. This is because the methods mentioned above require comonomers with largely different ROMP activity, except in the case of enantioselective ROMP of racemic 1-methylnorbornene.

Scheme 1. Alternating Copolymerization of **1** and **2**



We have reported that amino acid bifunctionalized norbornene derivatives efficiently undergo ROMP to give polymers with fairly high molecular weights in good yields.[40] The polymerization proceeds in a living fashion to some extent, and the polymerizability of the monomers largely depends on the substituents, stereostructure (*endo*- and *exo*-), solvents, and catalysts. A norbornene monomer having amino acid derived carboxy groups successfully undergoes ROMP with the Grubbs second generation Ru catalyst. The carboxy groups need no protection,[41] presumably because the spacer between the norbornene ring and the carboxy groups prevents the carboxy groups from interacting with the Ru center of the catalyst, which is coordinated at the double bond in the metathesis intermediate. This is also operative in the ROMP of norbornene monomers having amino acid derived nonprotected amino groups, wherein *N*-methyl substitution is effective in enhancing the polymerizability.[42] In the course of our study on the ROMP of such acidic and basic norbornene monomers, we considered trying alternating copolymerization utilizing acid−base interactions. The present article describes the alternating ring-opening metathesis copolymerization of an amino acid derived monomer having carboxy groups (**1**) with a monomer having amino groups (**2**) using the Grubbs Ru catalyst as illustrated in Scheme 1.

Results and Discussion

Monomer Synthesis. *N*-Methyl-L-phenylalanine derived *exo*,*exo*-disubstituted novel norbornene monomer **2** having nonprotected amino groups was synthesized from the *N*-Boc-protected precursor (**2-Boc**) by deprotection using TFA, followed by neutralization with a base as illustrated in Scheme 2. EDC·HCl was employed as a condensation agent because the urea derivative can be easily removed from the reaction mixture by washing with water.[40] The monomer structure was deter-

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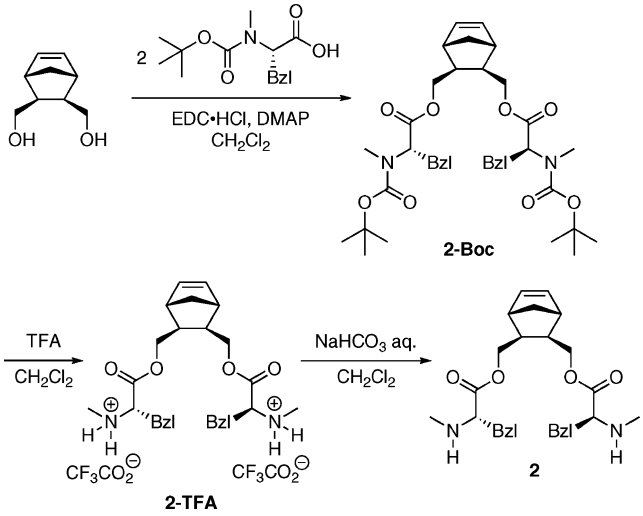
Scheme 2. Synthesis of Monomer **2**



mined by IR, ^{1}H, and ^{13}C NMR spectroscopies, as well as by high resolution mass spectrometry.

Homopolymerization. The homopolymerizations of monomers **1** and **2** were carried out with the Grubbs second generation Ru catalyst (2.0 mol %) in DMF-d_7 at 50 °C while monitoring the conversions by ^{1}H NMR spectroscopy. The conversions of monomers **1** and **2** were calculated from the integration ratios of the olefinic protons (6.21 and 6.03 ppm) with those of the polymers (5.29−5.52 and 5.27 ppm), respectively. Monomer **2** polymerized faster than **1** as plotted in Figure 1a. The M_n's of isolated poly(**1**) and poly(**2**) were 4700 and 11 000, as listed in Table 1.

Copolymerization. The copolymerization of **1** and **2** was carried out at a feed ratio of 1:1 under the same conditions as those for the homopolymerizations. Monomers **1** and **2** were converted at the same rate [Figure 1b], which was intermediate between the rates of the homopolymerizations [Figure 1a]. The first-order kinetic plots (Figure S2) revealed that the rate constants of homopolymerizations of **1** and **2** [Figure 1a] and copolymerization of **1** and **2** at a ratio of 1:1 [Figure 1b] were 0.61×10^{-2}, 3.75×10^{-2}, and 2.29×10^{-2} s^{-1}, respectively.

Copolymerizations of **1** and **2** were also carried out at feed ratios of 1:2 and 2:1. In the former case, the conversion of monomer **2** was half of that of **1** at all times, as plotted in Figure 2a. In the latter case, the conversion of monomer **1** was half of that of **2** at all times, as plotted in Figure 2b. Thus, equimolar amounts of monomers were consumed in both cases, suggesting that 1:1 copolymerization took place.

Figure 3a demonstrates the relationship between the feed and unit ratios of monomer **1** in the copolymers obtained at 10% conversion in the copolymerizations. The monomer unit ratios were calculated from the conversion of each monomer. The unit ratio of **1:2** was 50:50 in the copolymer when the feed ratio was 50:50. The unit ratios remained almost the same, irrespective of the feed ratios, which ranged from 17:83 to 83:17. Alternating copolymerization was further verified by monomer reactivity ratios ($r_1 = 0.08$, $r_2 = 0.02$), which were calculated by the Fineman−Ross method.[43] The values were close to zero, indicating that the copolymerization proceeded alternatingly.[36b,44] Figure 3b depicts the relationship between the feed and unit

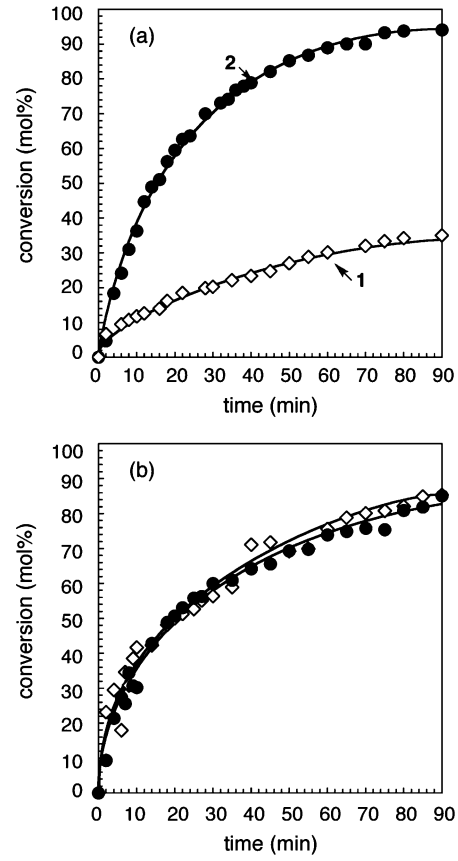


Figure 1. (a) Time−conversion plots of the homopolymerizations of **1** (◇) and **2** (●). (b) Time−conversion plots of the copolymerization of **1** (◇) and **2** (●) at a ratio of 1:1. Conditions: $[M]_{0,total} = 0.11$ M, $[M]_0$/[catalyst] = 50 in DMF-d_7 at 50 °C.

Table 1. Homo- and Copolymerizations of **1** and **2**[a]

feed ratio (mol %)					unit ratio[b] (mol %)	
1	**2**	total conversion[b] (mol %)	M_n[c]	M_w/M_n[c]	**1**	**2**
100	0	36	4700	1.26	100	0
83	17	31	5300	1.67	76	24
67	33	68	7100	1.41	57	43
50	50	78	9400	1.51	50	50
33	67	59	7000	1.69	45	55
17	83	35	5600	1.40	25	75
0	100	89	11 000	1.50	0	100

[a] Conditions: $[M]_{0,\ total} = 0.11$ M, $[M]_0$/[catalyst] = 50 in DMF-d_7 at 50 °C for 60−90 min. [b] Determined by ^{1}H NMR. [c] No elution peaks could be observed when the samples of poly(**1**) and poly(**1**-*co*-**2**)s were analyzed by GPC (DMF, 10 mM LiBr). To facilitate elution, the carboxy groups were transformed into the corresponding methyl esters using $TMSCHN_2$ prior to GPC separation.

ratios of **1** in the copolymers obtained after the copolymerization for 15 min (20−45% conversion). Although the deviation of the unit ratio became large from 50:50 compared to Figure 3a, it still exhibited the alternating character.

The M_n's of the copolymers ranged from 5300 to 9400 ($M_w/M_n = 1.40-1.69$) as listed in Table 1. The yield and M_n of the copolymer were maximum at a monomer feed ratio of 50:50, as shown in Figure 4. This result clearly indicates that the acidic and basic monomers interact most efficiently

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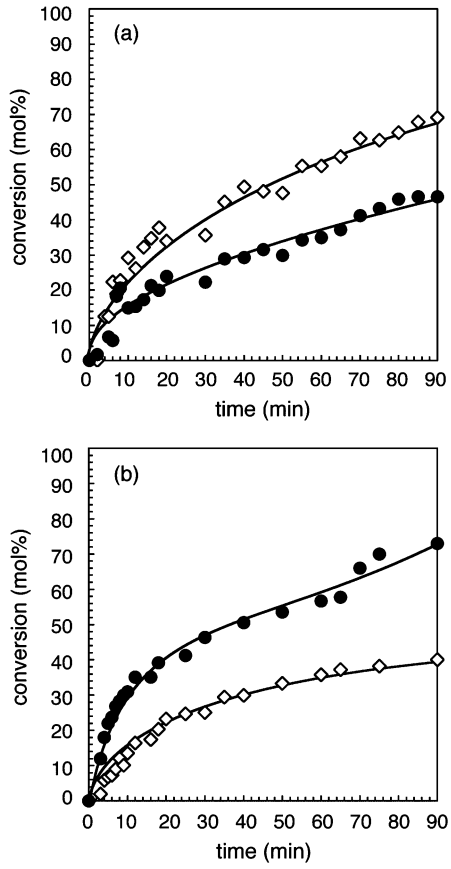


Figure 2. Time−conversion plots of the copolymerizations of **1** (◇) and **2** (●) at ratios of (a) 1:2 and (b) 2:1. Conditions: $[M]_{0,total} = 0.11$ M, $[M]_0$/[catalyst] = 50 in DMF-d_7 at 50 °C.

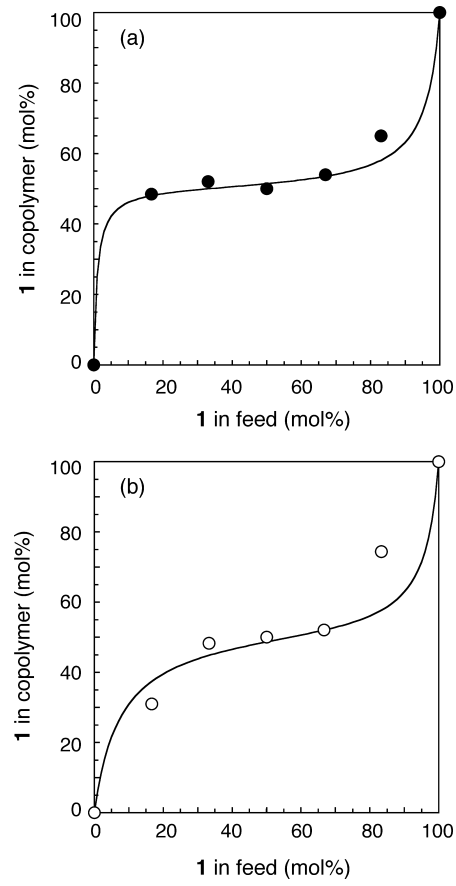


Figure 3. Relationships between the contents of **1** in copolymer and monomer feed in the copolymerization of **1** and **2**. (a) Conditions: $[M]_{0,total}$ = 0.11 M, $[M]_{0,total}$/[catalyst] = 50 in DMF-d_7 at 50 °C at ca. 10% conversions. $r_1 = 0.08$, $r_2 = 0.02$. (b) For 15 min, conversions 20−45%. $r_1 = 0.08$, $r_2 = 0.14$. The lines through the data points are theoretical, based on the r_1 and r_2 values.

when the molar ratio is 1:1. Alternating character is also observed in the radical copolymerization of acidic and basic vinyl monomers, such as 2-acrylamido-2-methyl-1-propanesulfonic acid (APSA) and 1-vinylimidazole (1-VIm).[45] But in that case, it is concluded that acceptor−donor interaction between APSA and 1-VIm seems more important than an acid−base interaction, because the combination of styrene-4-sulfonic acid (SSA) and 1-VIm does not undergo alternating copolymerization. Thus, the large difference of electronic character of the double bonds in APSA and 1-VIm plays an important role, instead of acid−base interactions. On the other hand, the difference of electronic character between the present monomers **1** and **2** is small; the net atomic charges of olefin carbon atoms of **1** and **2** were calculated to be −0.124 and −0.136.[46] It is therefore considered that acid−base interaction is the key factor in alternation of the copolymerization of **1** and **2**.

It is likely that the acid−base interaction between monomers **1** and **2** affects the polymerization rate. To confirm that acid−base interaction is responsible for the alternating copolymerization of **1** and **2**, the copolymerization of amine monomer **2** and ester monomer **3** (Chart 1) was carried out for comparison under the same conditions as those of the copolymerization of **1** and **2**. Figure 5 depicts the relationship between the monomer feed and content of **2** in the copolymer at 11−13% conversions. The content of **2** in copolymer increased almost linearly with increasing content of **2** in feed, which demonstrates that the copolymerization of **2** and **3** did not take place alternatingly but rather that random copolymerization occurred. The monomer reactivity ratios of **2** and **3** were

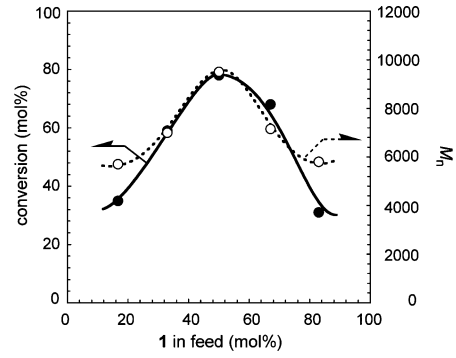
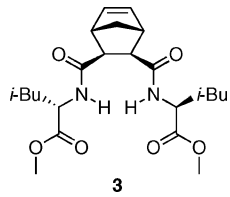


Figure 4. Total monomer conversion (●) and M_n (○) of the product copolymers as a function of the content of monomer **1** in the feed in the copolymerization of **1** and **2**.

(46) The calculation was carried out by the semiempirical molecular orbital method using the AM1 Hamiltonian, running on Wavefunction Inc. Spartan '08 for Windows version 1.1.1.

(47) The ^{1}H NMR spectra of mixtures of monomers **1** and **2** were measured at various compositions to verify the existence of an interaction between them. As depicted in Figure S1, the−CO_2H signal of **1** gradually broadened and shifted from 12.3 ppm to higher field upon raising the content of **2**. On the other hand, the−NH−signal of **2** gradually broadened and shifted from 9.2 ppm to lower field upon raising the content of **1**. The−CO_2H and−NH−signals coalesced when **1** and **2** were mixed. These results indicate that the carboxy and amino groups of monomers **1** and **2** undergo an acid/base interaction.

Chart 1. Structure of Monomer **3**



3

calculated to be 0.60 and 1.02 at 11−13% conversions by the Fineman−Ross method. These results confirm the randomness of the copolymerization of **2** and **3**, along with the importance of the acid−base interaction for the alternating copolymerization of **1** and **2**.

Figure 6a illustrates the acid−base interaction between the carboxy and amino groups of **1** and **2**[47] which enhances the

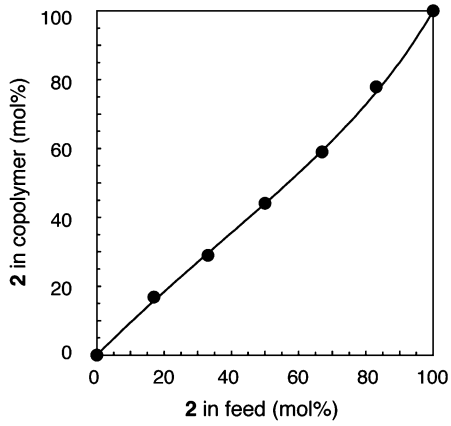


Figure 5. Relationship between the contents of **2** in copolymer and monomer feed in the copolymerization of **2** and **3**. Conditions: $[M]_{0,total}$ = 0.11 M, $[M]_{0,total}$/[catalyst] = 50 in DMF-d_7 at 11−13% conversions, r_1 = 0.60, r_2 = 1.02. The line through the data points is theoretical, based on the r_1 and r_2 values.

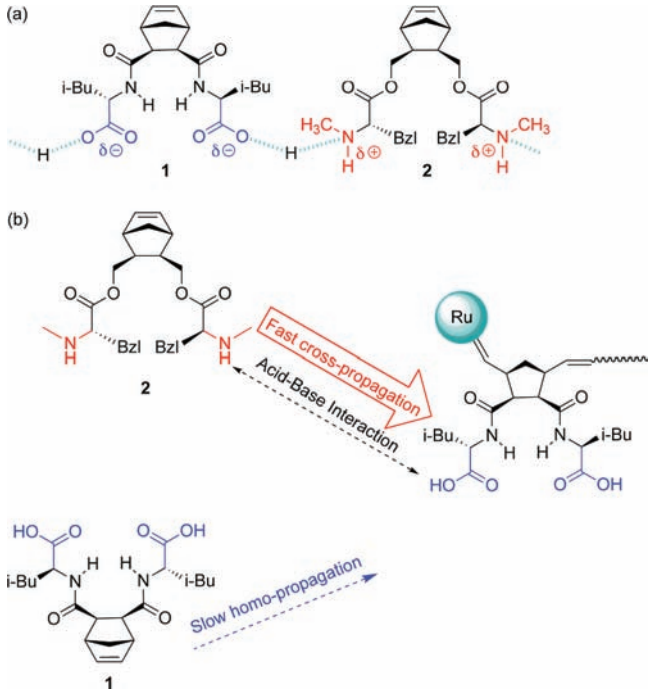


Figure 6. Probable mechanisms for alternating copolymerization. (a) Acid−base interaction between monomers that enhances the local monomer concentration. (b) Acid−base interaction between the metal carbene propagating species and the incoming monomer.

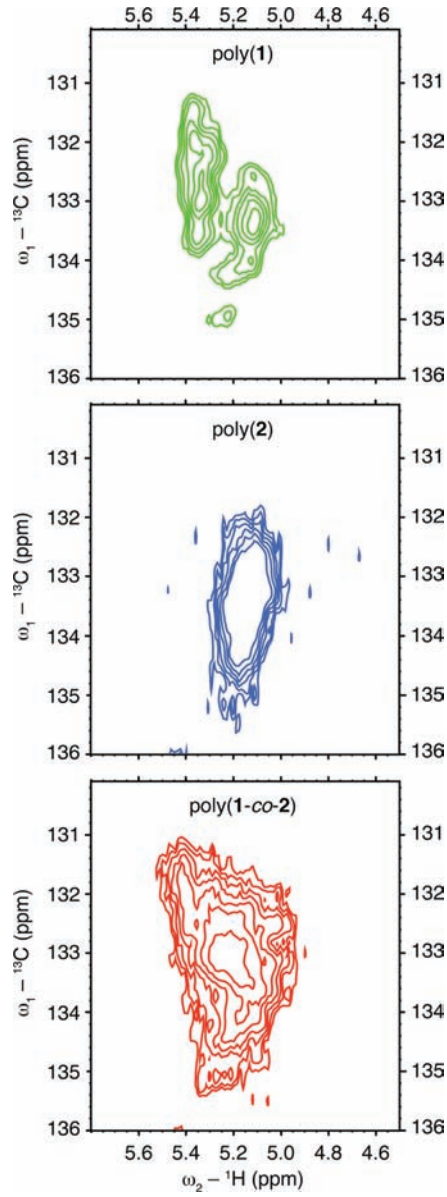


Figure 7. Olefinic region of $^1H-^{13}C$ HSQC NMR spectra (700 MHz) of poly(**1**), poly(**2**), and poly(**1**-*co*-**2**) measured in DMSO-d_6 at 35 °C.

local monomer concentration to bring about the alternating copolymerization of the monomers. Another possibility is an acid−base interaction between the metal carbene propagating species and the incoming monomer. As illustrated in Figure 6b, it is likely that the monomer **1** derived metal carbene moiety preferably interacts with the amino groups of monomer **2** rather than with the carboxy groups of monomer **1** due to an acid−base interaction, leading to the alternating copolymerization. In a similar fashion, a monomer **2** derived propagating end preferably reacts with monomer **1** rather than **2**. By contrast, such acid−base interaction does not exist between monomers **2** and **3**. Consequently, it is considered that **2** does not copolymerize with **3** alternatingly but that random copolymerization occurs.

One-dimensional ^{13}C NMR spectra of the polymers did not provide useful structural information, because the olefinic carbon signals of the homopolymers and copolymer appeared at the same position. We therefore measured the $^1H-^{13}C$ HSQC (Heteronuclear Single Quantum Coherence) spectra of the polymers using a 700 MHz NMR spectrometer, to

Table 2. Solubility of the Polymers[a]

solvent	polymer		
	poly(**1**)	poly(**2**)	poly(**1**-*co*-**2**)
hexane	−	−	−
toluene	−	−	−
$CHCl_3$	−	−	−
CH_2Cl_2	−	−	−
THF	+	+	−
acetone	−	+	−
MeOH	+	+	+
DMF	+	+	+
DMSO	+	+	+
H_2O	−	+	−
HCl (1 M)	−	+	−
NaOH aq. (1 M)	+	−	+

[a] −: insoluble, +: soluble.

observe differences in the signal shapes of the olefinic regions of the homopolymers compared to the copolymer. As shown in Figure 7, the olefin signal of poly(**1**-*co*-**2**) is different from those of poly(**1**) and poly(**2**), especially from that of poly(**2**). Since the pattern of the copolymer signal was not a simple sum of those of the homopolymers, it is considered that the copolymer contains a unit sequence other than the homosequences of monomer units **1** and **2**. The alternating dyads could not be calculated due to the almost identical chemical shifts of the homo- and copolymers.

Table 2 gives solubility data for the homopolymers and alternating copolymer. Both of the homopolymers are insoluble in low-polarity solvents like hexane, toluene, CH_2Cl_2, and $CHCl_3$, but they are soluble in polar solvents, including THF, MeOH, DMF, and DMSO. Poly(**1**) having carboxy groups was insoluble and soluble in HCl and NaOH aq., respectively, while poly(**2**) having amino groups was soluble and insoluble in HCl and NaOH aq., respectively, as predicted from the functional groups. Poly(**2**) was also soluble in neutral H_2O. The solubility of poly(**1**-*co*-**2**) was the same as that of poly(**1**) except in THF. The interaction of the carboxy groups with solvents seems to be more pronounced compared to the amino−solvent interaction.

Conclusions

In this paper, we have demonstrated that norbornene monomer **1** having carboxy groups and monomer **2** having amino groups successfully undergo alternating copolymerization. The key factor favoring alternating copolymerization seems to be acid−base interaction between the monomers, leading to enhancement of local monomer concentration, and acid−base interaction between the metal carbene propagating species and the incoming monomer. This reasoning is supported by ^{1}H NMR spectroscopic analysis and a control experiment, in which **2** was copolymerized with monomer **3** having ester-protected carboxy groups. As far as we know, the present study is the first successful example of an alternating ring-opening metathesis copolymerization between two kinds of norbornene monomers substituted with different functional groups. We believe that our achievement contributes not only to the development of well-defined ROMP chemistry but also to the enhancement of properties of ROMP-based polymers.

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Supporting Information Available: Experimental procedures, ^{1}H NMR spectra of mixtures of **1** and **2** with various compositions (Figure S1), relationships between $\ln([M]_0/[M])$ and time in the homopolymerizations of **1** and **2** and in the copolymerization of **1** and **2** at a ratio of 1:1 (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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