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Hiroshi Tamura^a; Narinobu Maeda^a; Rumi Matsumoto^a; Atsushi Nakayama^a; Hiroki Hayashi^a; Kenji Ikushima^a; Minoru Kuraya^a

^a Faculty of Engineering, Kansai University and High Technology Research Center, Osaka, Japan

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Hiroshi Tamura,* Narinobu Maeda, Rumi Matsumoto,
Atsushi Nakayama, Hiroki Hayashi, Kenji Ikushima,
and Minoru Kuraya

Faculty of Engineering
Kansai University and
High Technology Research Center
3-3-35 Yamate-cho, Suita
Osaka 564-8680, Japan

Key Words: Metathesis, ADMET Polymerization, Grubbs Catalyst, Telechelic Polymer

ABSTRACT

Ester terminated telechelic polymers were synthesized by the Acyclic Diene METathesis (ADMET) polymerization of 1,9-decadiene with ester-containing monoolefins using ruthenium based Grubbs catalyst. The number of methylene spacers between the olefin and the ester from the oxygen side of the ester-containing monoolefins were varied from one to three. The optimal condition of the present ADMET polymerization was determined as monomer/catalyst ratio of 400/1 for 72 hours at 90°C. All polymer structures were characterized by FT-IR and ¹H-NMR spectroscopy. It is quite interesting that even allyl *n*-butyrate with one methylene spacer metathesizes successfully using ruthenium catalyst despite this monoolefin suffers stronger negative neighboring group effect than the other monoolefins. Mechanism of the ADMET polymerization of 1,9-decadiene

* Author to whom correspondence should be addressed.

with ester-containing monoolefin was examined comparing the reactions for each of the monomers. Deprotection of terminal ester group was successful to give alcohol terminated telechelic polymer which is useful for production of block copolymer.

INTRODUCTION

The finding of well-defined organometallic catalysts have resulted in the great progress in metathesis chemistry. Tungsten and molybdenum based Schrock catalysts [1, 2] made a bridgehead on it. These catalysts allow ring-opening metathesis polymerization [3] (ROMP) and ring closing metathesis [4] (RCM) reactions. The success of living polymerization by ROMP offers a new methodology for polymer synthesis. However, complicated synthesis of preferable cyclic monomer for ROMP limits the general application of ROMP. Recently, Wagener *et al.* reported a new type metathesis chemistry, acyclic diene metathesis (ADMET) polymerization using Schrock catalyst [5], as well as ruthenium based Grubbs catalyst [6]. ADMET polymerization is a useful method polymerizing various kinds of functionalized olefins to produce polymer which are perfectly linear and free from branching and other defects [7-10].

Telechelic polymer is a very useful intermediate material for the production of functional polymer. Much research for telechelic polymer covers the whole area of polymer synthesis methods [11-13]. Well-defined acetate terminated telechelic poly(butadiene) has been prepared by living ring-opening metathesis polymerization of 1,5-cyclooctadiene with a chain transfer agent [14, 15]. Recently, Wagener *et al.* reported the synthesis of telechelic polymer by ADMET depolymerization [16] and polymerization [17].

This paper describes the synthesis of ester terminated telechelic polymer by ADMET polymerization of 1,9-decadiene with ester-containing monoolefins using Grubbs catalyst. The optimal conditions and mechanism of ADMET polymerization were examined. The deprotection of ester moiety was successfully achieved to give alcohol terminated telechelic polymer.

EXPERIMENTAL

Materials

Grubbs' ruthenium catalyst was synthesized according to the literature method [18]. 1,9-Decadiene (**1**) and allyl *n*-butyrate (**2**) were purchased from

Wako Pure Chemical Industries, Ltd. Other ester-containing monoolefins, 3-butenyl *n*-butyrate (**2**) and 4-pentenyl *n*-butyrate (**4**), were synthesized by the esterification of *n*-butyryl chloride with corresponding olefin alcohol. They were dried over calcium hydride and transferred into a round bottomed flask equipped with a high vacuum Teflon stopcock prior to use.

Polymerization

The polymerization was performed under reduced pressure at 90°C for 72 hours with a mole ratio of monomer/catalyst = 400/1. The ratio of diene/monoolefin was adjusted to 5/1. Ethylene as a by-product was removed every 3 hours from the reaction system, and the reaction was finished by exposing the reaction mixture to the air. The reaction mixture was dissolved in a small quantity of toluene, precipitated from methanol, and dried *in vacuo*.

Allyl n-butylate Endcapped Telechelic Polymer (5)

Viscous oil. Yield: 20%. ¹H-NMR (CDCl₃): δ 0.95 (t, ³J_{HH}=7.2Hz, -CH₃), 1.21-1.41(m, =CH-CH₂-(CH₂)₄-), 1.58-1.61 (m, -CH₂-CH₃), 1.94-2.05 (m, =CH-CH₂-), 2.29 (t, ³J_{HH}=7.2Hz, -OCO-CH₂-), 4.51 (d, ³J_{HH}=6.4Hz, =CH-CH₂-O), 5.30-5.42 (m, -CH=CH-), 5.50-5.65 (m, -CH=CH-). Anal. Calcd. For C₂₅₆H₄₄₈O₄ (Mn = 3490): C, 85.63; H, 12.59. Found: C, 86.16; H, 12.54.

3-Butenyl n-butylate Endcapped Telechelic Polymer (6)

Viscous oil. Yield: 28%. ¹H-NMR (CDCl₃): δ 0.95 (t, ³J_{HH}=7.2Hz, -CH₃), 1.25-1.39 (m, =CH-CH₂-(CH₂)₄-), 1.59-1.61 (m, -CH₂-CH₃), 1.90-2.06 (m, =CH-CH₂-), 2.27 (t, ³J_{HH}=7.2Hz, -OCO-CH₂-), 4.08 (d, ³J_{HH}=6.4Hz, =CH-CH₂-CH₂-O), 5.32-5.44 (m, -CH=CH-), 5.45-5.55 (m, -CH=CH-). Anal. Calcd. For C₂₃₄H₄₁₀O₄ (Mn = 3210): C, 85.47; H, 12.58. Found: C, 85.95; H, 12.54.

4-Pentenyl n-butylate Endcapped Telechelic Polymer (7)

Viscous oil. Yield: 36%. ¹H-NMR (CDCl₃): δ 0.95 (t, ³J_{HH}=7.2Hz, -CH₃), 1.27-1.37 (m, =CH-CH₂-(CH₂)₄-), 1.59-1.63 (m, -CH₂-CH₃), 1.64-1.70 (m, =CH-CH₂-CH₂-CH₂-O), 2.28 (t, ³J_{HH}=7.2Hz, -OCO-CH₂-), 4.06(d, ³J_{HH}=6.4Hz, =CH-CH₂-CH₂-CH₂-O), 5.30-5.44 (m, -CH=CH-). Anal. Calcd. For C₄₁₀H₇₂₂O₄ (Mn = 5640): C, 86.14; H, 12.74. Found: C, 86.58; H, 12.69.

Deprotection of the Telechelic Polymer

Ester terminated telechelic polymer (**7**) was treated with sodium hydroxide in H₂O-EtOH under reflux for 24 hours. The reaction mixture was neutral-

ized, extracted with chloroform, and evaporated. The crude product was redissolved in a small quantity of chloroform, precipitated from acetone, and dried *in vacuo*.

Alcohol Endcapped Telechelic Polymer (7)

Viscous oil. Yield: 80%. ¹H-NMR (CDCl₃): δ 1.20-1.40(m, =CH-CH₂-(CH₂)₄-), 1.89-2.04(m, =CH-CH₂-), 3.66(s, -OH), 5.30-5.45(m, -CH=CH-). Anal. Calcd. For C₃₆₈H₆₄₆O₂ (Mn = 5400): C, 86.61; H, 12.76. Found: C, 86.22; H, 12.82.

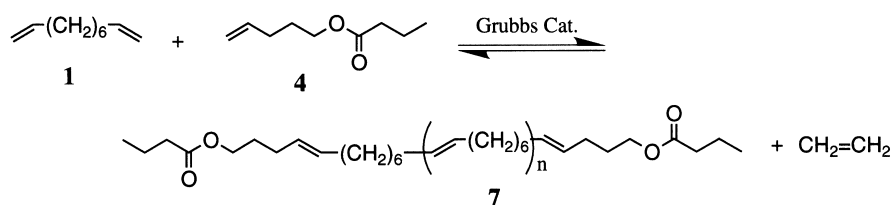
Measurements

Proton NMR spectrum was obtained with a JOEL JNM-EX270 superconducting spectrometer system. FT-IR spectra were measured with a Perkin Elmer PARAGON 1000 FT-IR spectrometer. Gel permeation chromatography (GPC) data (relative to polystyrene standards) were collected using a Toso HLC 8020 liquid chromatography apparatus equipped with a refractive index detector and TSKgel G2000H_{HR} and G3000H_{HR} columns.

RESULTS AND DISCUSSION

Optimal Conditions

In order to explore the optimal conditions, polymerization of 1,9-decadiene (**1**) with 4-pentenyl *n*-butyrate (**4**) was performed under several conditions (Scheme 1). Although there are several ways to evaluate the optimal conditions (yield etc.), molecular weight of the polymer was evaluated as an index of the optimal condition because this value can be measured during the course of the polymerization. At first, reaction temperature was varied under monomer/catalyst = 400/1 and diene/monoene = 5/1. Sampling of the reaction mixture (100 μL) was done every 24 hours. This solution was diluted with THF and measured by GPC after passing through the membrane filter with the pore size of 0.45 μm. Typical example of GPC trace of the telechelic polymer (**7**) measured after the reaction at 90°C for 72 hours is shown in Figure 1a. Figure 1a demonstrates that reaction mixture contains variety of molecular weight components since ADMET polymerization is a step reaction. Thus, in this section, molecular weight of the polymer was represented as the value indicated by the arrow shown in the Figure 1a.



Scheme 1. ADMET copolymerization of 1,9-decadiene **1** with 4-pentenyl *n*-butyrate **4**.

Figure 2 shows the effect of reaction temperature on molecular weight of the telechelic polymer (**7**). Molecular weight of the polymers reached the maximum value and it decreased by the prolonged reaction in all the tested temperatures. Maximum value at 90°C was 5060 after 72 hours and that at 80 and 100°C was 3240 and 2440 after 48 hours, respectively. This result suggests that

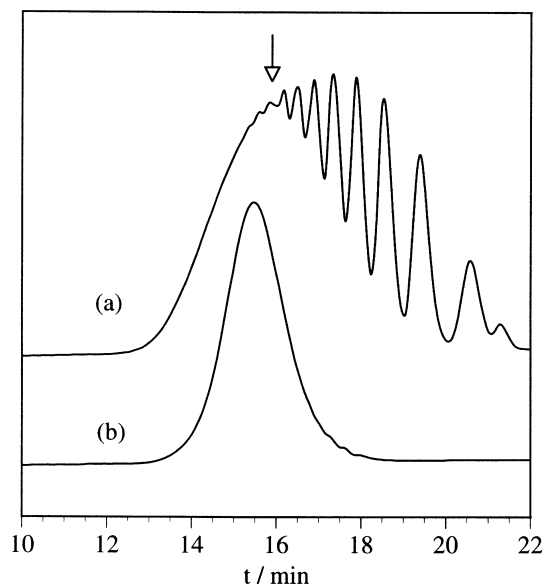


Figure 1. GPC traces of the telechelic polymer of reaction mixture at 90°C for 72 hours (a) and reprecipitated sample (b). Molecular weight of the polymer described in the section of optimal condition of the polymerization is represented as the value indicated by the arrow.

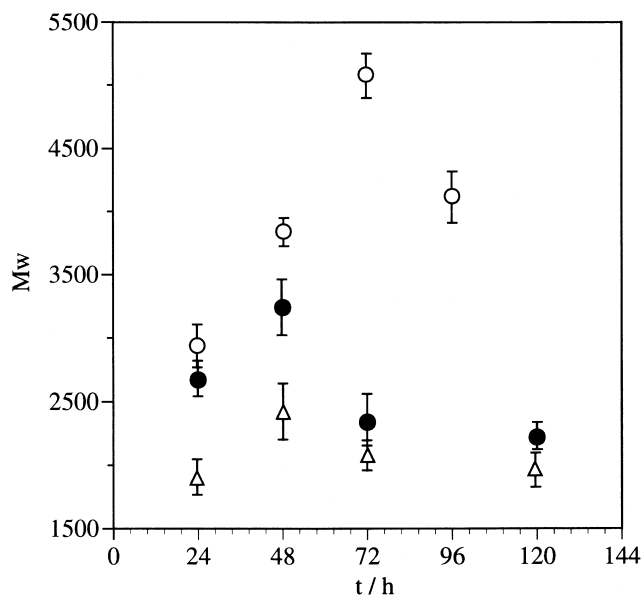


Figure 2. Effect of temperature on molecular weight of the telechelic polymer **7**.
 ●: 80°C, ○: 90°C, △: 100°C.

Grubbs catalyst is most effective at 90°C for ADMET polymerization in the present system of which the temperature is higher than that reported by Wagener *et al.* (70°C) [6].

The effect of the monomer/catalyst ratio on molecular weight of the telechelic polymer **7** examined at 90°C is shown in Figure 3. The ratio of diene/monoene was kept at 5/1. Molecular weight of the polymer approached the maximum value of 3000 as the reaction time increased when the monomer/catalyst ratio was adjusted to 200/1 and 800/1. On the contrary, Mw value reached the maximum value of 5060 after 72 hours in the case of 400/1.

Thus, optimal condition of the present polymerization was determined as monomer/catalyst ratio of 400/1 for 72 hours at 90°C. The reprecipitation with toluene/methanol of the reaction mixture synthesized under the optimal condition gave the purified polymer of Mw = 8010, Mn = 5640 (Figure 1b). The present polydispersity of 1.42 is smaller than the theoretical value of 2, which is typical for step reaction.

Under the optimal condition, polymerizations were performed for 1,9-decadiene (**1**) with ester-containing monoolefins (**2-4**) in which the number of methylene spacers between the olefin and the ester from the oxygen side was

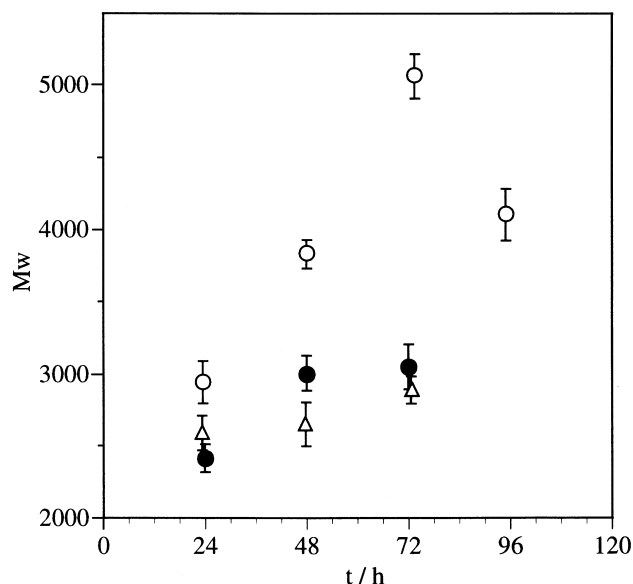


Figure 3. Effect of monomer/catalyst ratio on molecular weight of the telechelic polymer **7**. ●: 200/1, ○: 400/1, △: 800/1.

varied from one to three. The results are shown in Table 1. All the ester-containing monoolefins, even **2** with one methylene spacer, polymerized successfully using the ruthenium catalyst. This observation is in quite a contrast to the ADMET polymerization of an ester-containing monomer using molybdenum-based Schrock catalyst, where having less than two methylene spacers between the olefin and the ester moiety prevents polymerization [7]. Although molybde-

TABLE 1. Dimerization and Polymerization of Ester-Containing Olefins

Monomer	Dimerization	Polymerization		
	Conv./% ^{a)}	Conv./% ^{a)}	Mw	Mw/Mn
2	22.2	83.3	3910	1.12
3	66.9	88.2	3500	1.09
4	71.3	93.4	8010	1.42

a) Conversion was calculated from the decrease of monomer by ¹H-NMR.

num catalyst has high catalytic activity and provides high molecular weight polymer, this catalyst tends to suffer inhibition for polymerization due to the negative neighboring group effect [7]. This phenomenon was also found using the ruthenium catalyst demonstrated for the dimerization of ester-containing monoolefins (Table 1). The reactivity of the catalyst decreased with a decrease in the number of methylene spacers. However, ruthenium catalyst is still active for dimerization even with one methylene spacer (**2**). The molecular weight of the telechelic polymer (**5**) is around 3900, which increased with increasing the number of methylene spacer. Although the monomers are converted in high yield (83–93%), the isolated yield of the polymers were low (20–36%). It may be due to the loss during the reprecipitation procedure because molecular weights of the polymers are relatively low.

Structure of the Polymer

Figure 4 shows the $^1\text{H-NMR}$ spectrum of the reprecipitated ester terminated telechelic polymer (**7**) synthesized under the optimal conditions. Although the peak contributed to the proton i' cannot detect on the spectrum concealed behind that to proton c' , the spectrum contains both poly(1,9-decadiene) (f , c' , d' , e') and ester (j' - p') components. The peak area ratios contributed to poly(1,9-decadiene) and ester components are $f:c':d' = 1.0:1.9:3.8$ and $k':l':p' = 2.0:1.7:3.3$, respectively, which are in good agreement with expected values. The spectrum contains very strong internal olefinic peak (f ; 5.3–5.4 ppm) and almost no external olefinic peaks (5 and 5.8 ppm) from poly(1,9-decadiene) were found expanding the intensity at this region. The $^1\text{H-NMR}$ spectra of **5–7** in the internal olefinic region are shown in the Figure 5. Beside the strong internal olefinic peak (α), weak multiple peaks (β) were observed for **5** (5.50–5.65 ppm) and **6** (5.45–5.55 ppm). These peaks seem to be an internal olefinic peak adjacent to the ester oxygen, since they shift depending upon the distance between olefinic proton and ester oxygen. In addition, the position and shape of them were significantly different from those of dimers of ester-containing monoolefins (**2**; 5.7 and 5.9 ppm, **3**; 5.5 ppm). In the case of **7**, very weak and broad peaks appeared around 5.5–5.6 ppm. Considering the shift found in **5** and **6**, the peaks found in **7** are not assigned as an internal olefinic proton (h') and are still unknown. Thus, it is proper that the peaks from h' might be concealed behind the strong peak (f). Figure 6 shows the FT-IR spectra of purified **7** and **4**. The comparison of the spectra indicates the presence of ester group of band (1740 cm^{-1}) in the carbonyl stretching region. These results strongly suggest that the present polymer is an

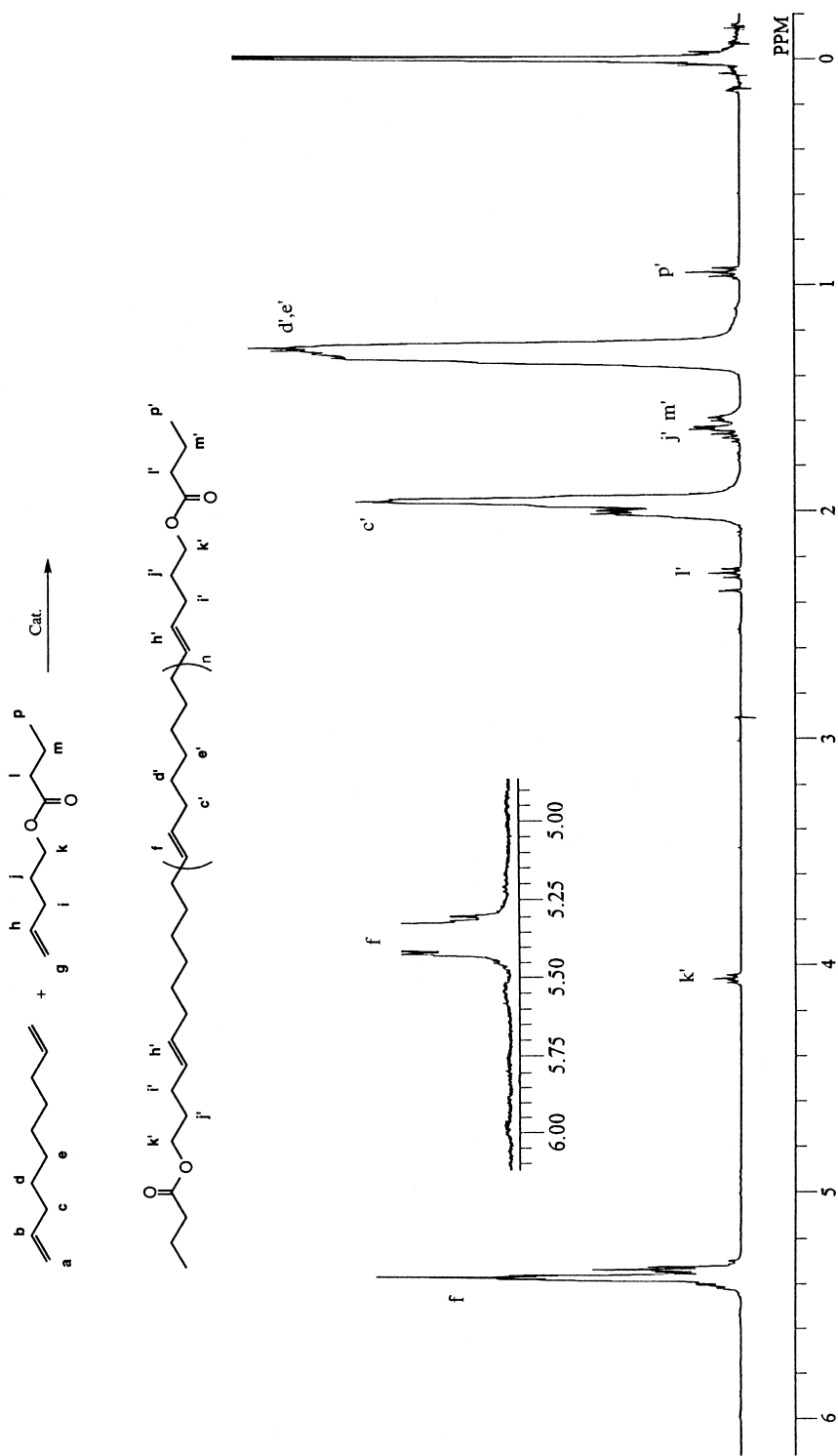


Figure 4. $^1\text{H-NMR}$ spectrum of ester terminated telechelic polymer 7.

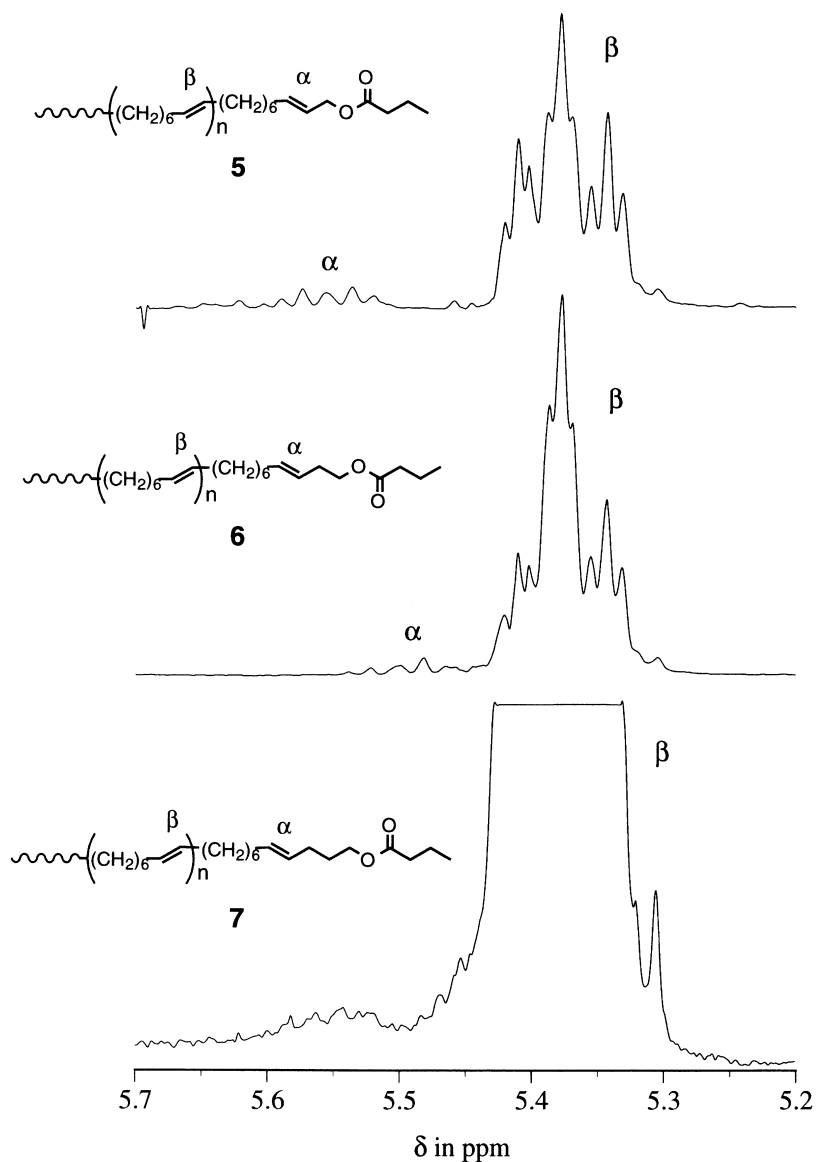


Figure 5. $^1\text{H-NMR}$ spectra of internal olefinic proton regions for ester terminated telechelic polymers.

objective ester terminated telechelic polymer with the poly(1,9-decadiene) backbone. The number average molecular weight (M_n) calculated from the peak area ratios of ester (k' , l' , p') and internal olefin (f) was 7900-6100, which was consistent with the GPC measurement ($M_n = 5640$).

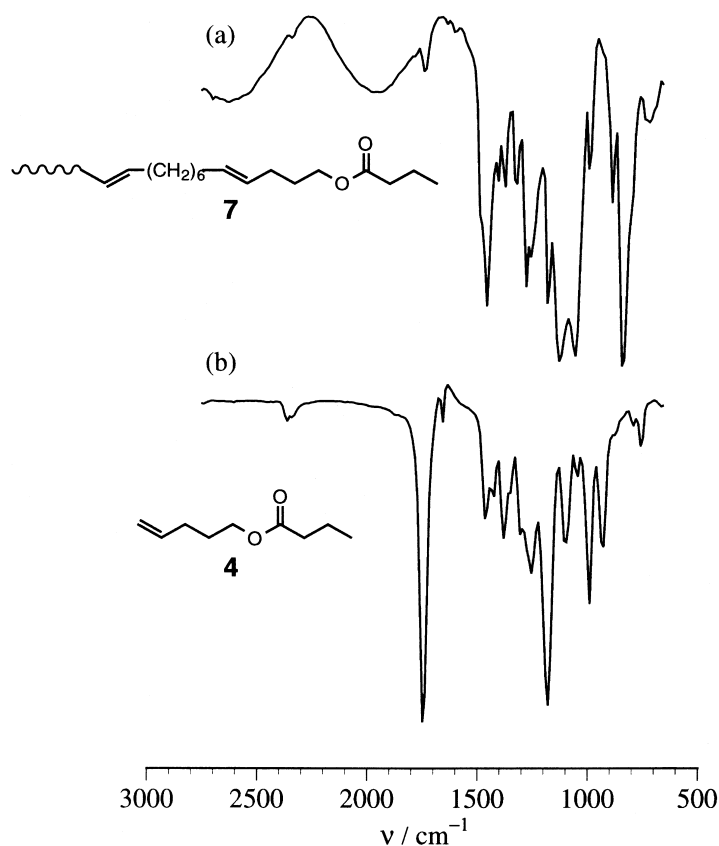


Figure 6. IR spectra of ester terminated telechelic polymer **7** (a) and monomer **4** (b).

Mechanism of the Polymerization

In order to investigate the polymerization mechanism, $^1\text{H-NMR}$ spectrum of polymerization of **1** with **2** was monitored because no overlap of internal olefinic peaks for dimer of **2** and other peaks were observed in this case. Conversions of monomers were calculated from the peak area of the $^1\text{H-NMR}$ spectra. The result is shown in Figure 7. For polymerization of **1** (\odot) and dimerization of **2** (\square), conversions reached 98 and 22% after 24 hours, respectively. In the course of the polymerization of **1** with **2**, no internal olefinic peaks for dimer of **2** were detected. Thus, we assumed that all the reacted **2** was introduced into the terminal of the polymer chain. The conversion of **2** in polymerization with **1** was monitored by the methylene proton adjacent to the ester oxygen (\blacksquare) as well

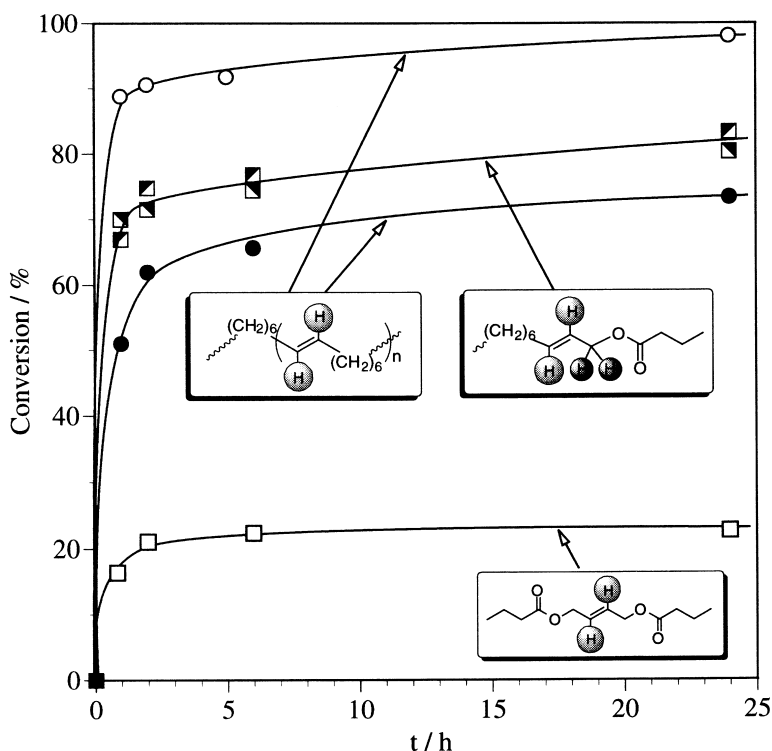
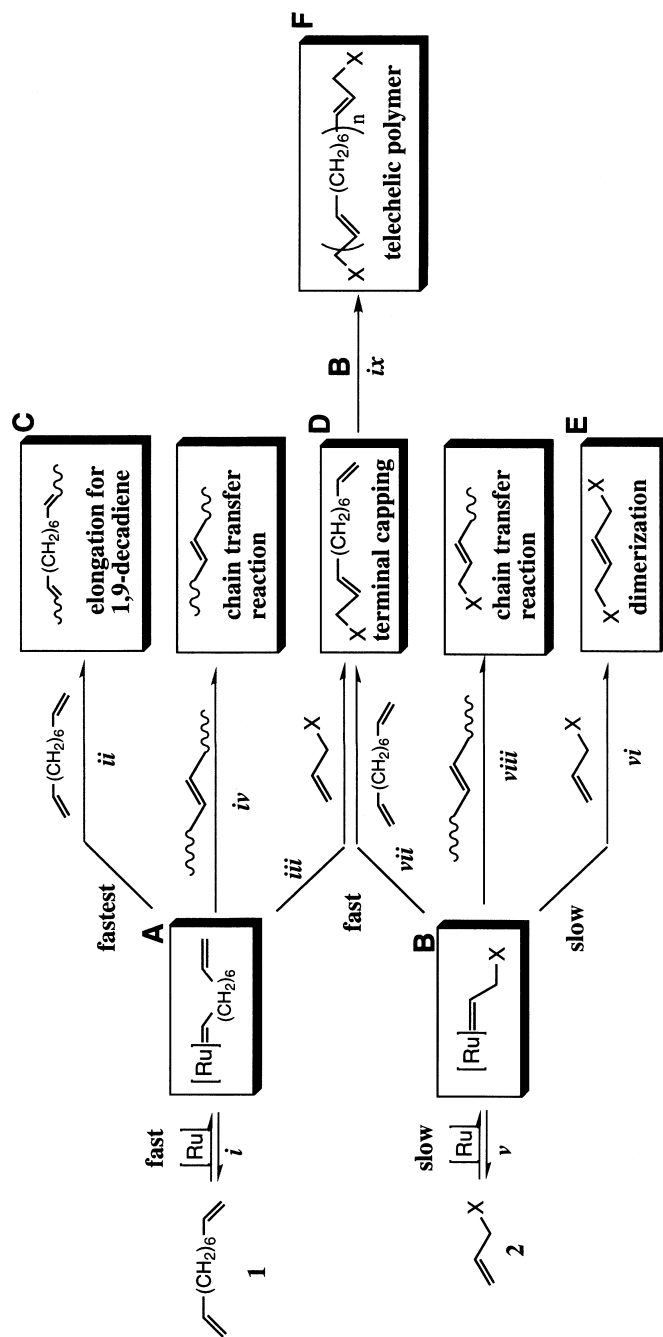


Figure 7. Time-conversion curves for polymerization of **1** (○), dimerization of **2** (□), and polymerization of **1** with **2**. For the polymerization of **1** with **2**, ● denotes conversion calculated from internal olefinic proton, ▣ and ▤ denote conversion calcu-

as the internal olefinic proton (▣). It is possible to distinguish between both *cis* and *trans* methylene proton adjacent to the internal olefinic proton in the telechelic polymer (**5**) by $^1\text{H-NMR}$ (Figure 8b), *i.e.*, the *cis* proton at 4.62 ppm and the *trans* proton at 4.51 ppm. A *trans* content of 74.7% is a value close to the reported value for the conventional ADMET polymerization [19]. The similar methylene proton in the dimer (Figure 8c) is also possible to distinguish between *cis* and *trans* (*trans* content; 79.2%). However, overlapping of *trans* peak of dimer at 4.60 ppm with that of monomer (**2**) makes it difficult to monitor the progress of the dimerization in stead of the use of internal olefinic proton (□). The conversion of **2** in polymerization with **1** (▣ and ▤) increased drastically compared to that in dimerization (□). This acceleration of the reactivity of

2 is quite interesting since this compound suffers higher negative neighboring group effect in polymerization compared to the other ester-containing monoolefins (Table 1). The fact that both the conversions obtained from internal olefinic (\blacksquare and methylene (\blacksquare) proton show the similar values indicates the proper assignment for the weak multiple peaks beside the strong internal olefinic peak. On the contrary, the reactivity of **1** with **2** in polymerization (\bullet) decreased compared to that of **1** in polymerization (\circ). Thus, speculated mechanism of ADMET polymerization is shown in Scheme 2.

Dimerization of **2** (pathways v and vi) is slower than polymerization of **1** (pathways i and ii) due to the negative neighboring group effect of **2**. Though **2** is consumed only by the pathways of v and vi when **2** is dimerized, **2** might be introduced into the terminal of the chain *via* other pathways of iii and vii when **2** is polymerized with **1**. These pathways (iii and vii) are crossmetathesis reaction of **1** with **2**, which enhance the consumption of **2** in the case of polymerization. According to the above results, relative reactivity decreases in the following order: polymerization of **1** (i , ii) > crossmetathesis reaction (i , iii , and v , vii) > dimerization of **2** (v , vi). Terminal capping by crossmetathesis of pathway iii precedes to pathway vii , since production of carbene species of **1** (A) might precede that of **2** (B). The decrease of reactivity of **1** in polymerization with **2** compared to that in polymerization of **1** (Figure 7; \bullet and \circ) may be demonstrated that crossmetathesis of **1** with **2** (Scheme 2; iii and vii) suffers from the negative neighboring group effect and internal olefin will disappear by the chain transfer reaction (Scheme 2; iv and $viii$). The main pathway for production of the telechelic polymer (F) is presumed to be ix since **2** crossmetathesizes with the other side of the external olefin of terminal capped species of D. There are two possible reactions in the pathway of ix ; one is carbene species like A produced by D crossmetathesizes with **2** and the other is carbene species B crossmetathesizes with D. It is not clear at this time which reaction is predominant. Before this final crossmetathesis reaction, repetition of the reactions of A toward D affords elongated terminal capped species of D, which leads increase of molecular weight. An internal olefins of elongated homopolymer (C), elongated terminal capped species (D) and telechelic polymer (F) might suffer from the attack of the carbene species of A or B, which is a chain transfer reaction. In the latter two cases, the attack of the carbene species of B produces telechelic polymer (F) where decrease of molecular weight of the polymer is expected [15]. Reactivity of chain transfer reaction may be inferior to that of the crossmetathesis reaction (pathway ix) as this reaction relates to internal olefin. The fact that no ADMET polymerization was found for 2,4-hexadiene, using ruthenium based Grubbs cat-



Scheme 2. Speculated mechanism of ADMET polymerization. In this case, X denotes OCOC_3H_7 .

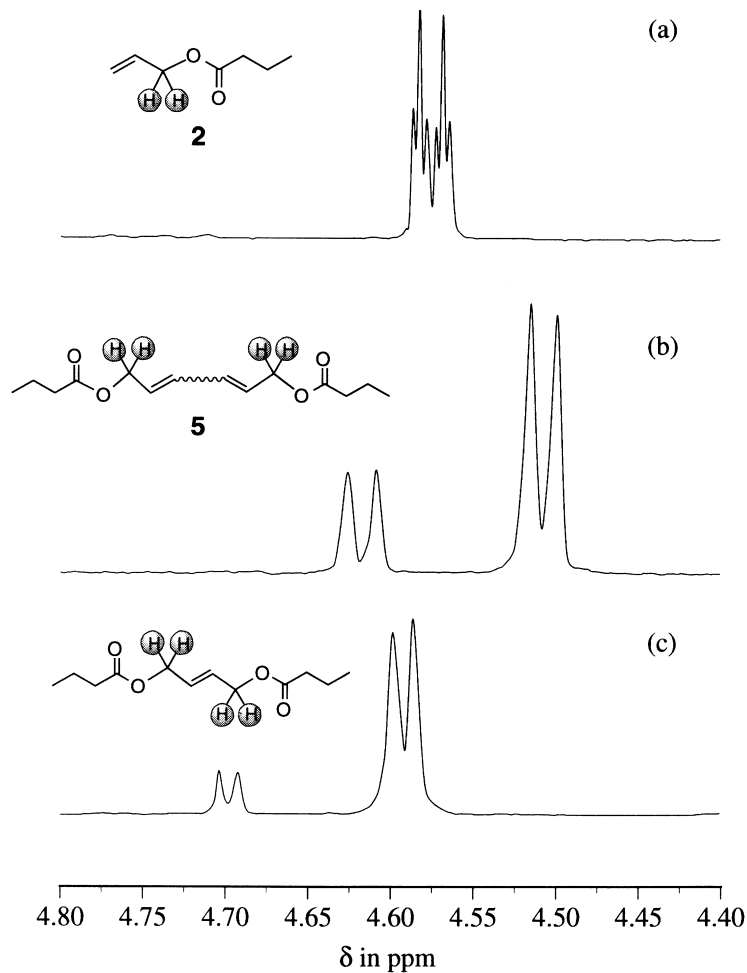


Figure 8. $^1\text{H-NMR}$ spectra of methylene proton adjacent to ester oxygen regions for monomer **2**, ester terminated telechelic polymer **5** and dimer of **2**.

alyst supports the above speculation. The decrease of molecular weight under the prolonged reaction time presented in Figures 2 and 3 might be due to this chain transfer reaction.

Deprotection of the Polymer

In order to improve the functionality of the ester terminated telechelic polymer, deprotection of terminal ester group was carried out. The treatment of ester terminated telechelic polymer (**7**) with sodium hydroxide in $\text{H}_2\text{O-EtOH}$

gave a highly viscous polymer. Figure 9 shows the $^1\text{H-NMR}$ spectra of ester terminated telechelic polymer (7) before and after the hydrolysis. Disappearance of the propyl portion (b, c, d) and a higher field shift of methylene proton from 4 ppm (a) to 3.6 ppm (a') suggests that the ester terminal was hydrolyzed to the corresponding alcohol terminal. The fact that methylene proton adjacent to hydroxyl group of monomeric penten-1-ol (3.7 ppm) supports the above result. Almost no molecular weight decrease was detected for the alcohol terminated telechelic polymer ($M_n=5400$) compared to that for ester terminated telechelic polymer (7) ($M_n=5640$), suggesting no degradation of the polymer backbone. Although the molecular weight of the present alcohol terminated telechelic polymer is relatively low, it is useful as a prepolymer for the production of block copolymer. Related work is now underway.

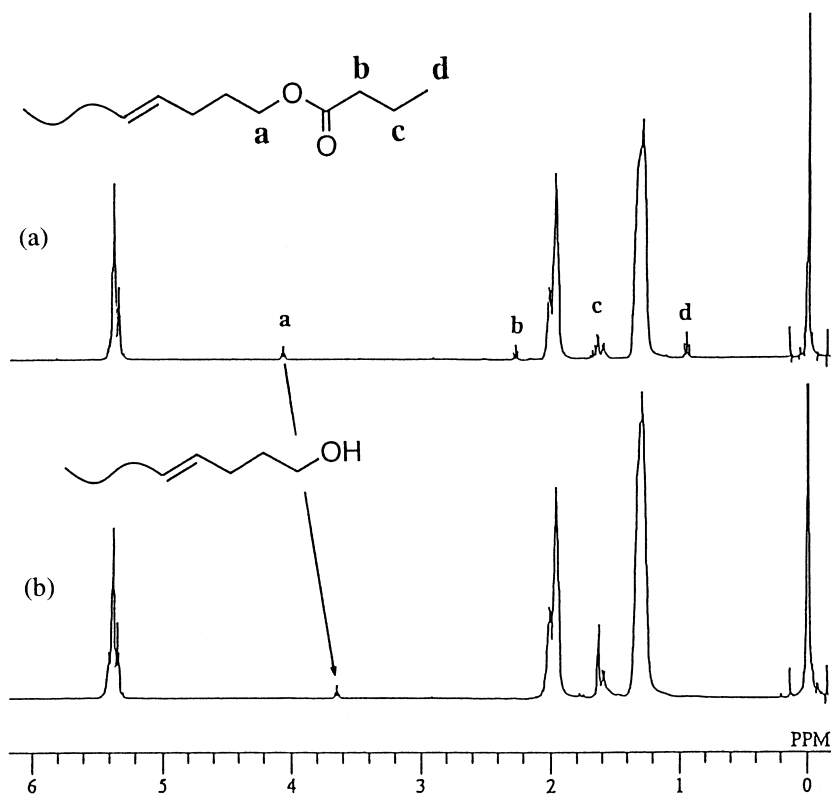


Figure 9. $^1\text{H-NMR}$ spectra of ester terminated telechelic polymer 7 before (a) and after (b) the hydrolysis.

CONCLUSION

ADMET polymerization of 1,9-decadiene with ester-containing monoolefins with various numbers of methylene spacers between the olefin and the ester using ruthenium based Grubbs catalyst was successfully achieved to give ester terminated telechelic polymers. The optimal condition of the present ADMET polymerization was determined as monomer/catalyst ratio of 400/1 for 72 hours at 90°C, which gave the polymer with weight-average molecular weight of 8010. Due to negative neighboring group effect, the molecular weights of the telechelic polymers depend on the number of methylene spacers of the ester-containing monoolefins. Examinations for the mechanism of the ADMET polymerization suggest that a main pathway for production of the telechelic polymer is presumed that ester-containing monoolefin crossmetathesizes with other side of the external olefin of terminal capped species. Terminal ester group of telechelic polymer was deprotected successfully to give a alcohol terminated telechelic polymer that is useful for production of block copolymer.

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