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## FUNCTIONAL TELECHELIC POLYMER SYNTHESIS VIA ADMET POLYMERIZATION

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### ABSTRACT

Acyclic Diene METathesis (ADMET) polymerization of 1,9-decadiene with epoxy-containing monoolefins using ruthenium based Grubbs' catalyst gave epoxy terminated telechelic polymers. The number of methylene spacers between the olefin and the epoxy from the oxygen side of the epoxy-containing monoolefins was varied from one to three. The optimal condition for the present ADMET polymerization was determined as monomer/catalyst ratio of 200/1 for 96 hr at 90°C. All polymer structures were characterized by FT-IR and <sup>1</sup>H NMR spectroscopy. It is quite interesting that even 1,2-epoxy-4-pentene with one methylene spacer metathesizes successfully using ruthenium catalyst despite this monoolefin suffers a stronger negative neighboring group effect than the other monoolefins. The telechelic polymer was reacted with toluene diisocyanate to give a higher molecular weight segmented copolymer connected with oxazolidone linkage.

*Key Words:* Metathesis; ADMET polymerization; Grubbs catalyst; Telechelic polymer; Epoxy

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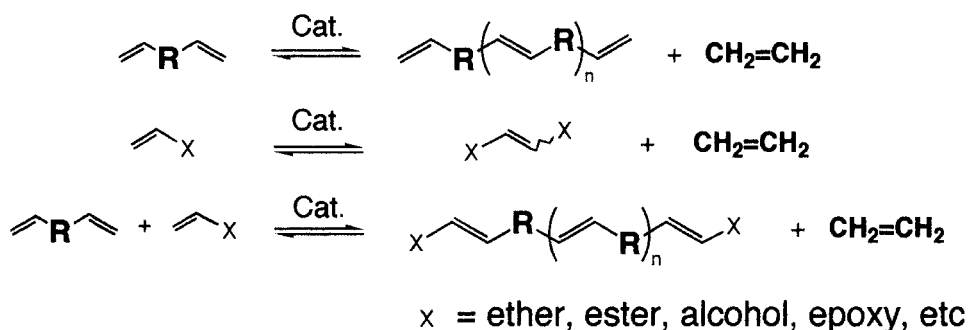
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## INTRODUCTION

Well-defined organometallic catalysts can be used in several types of metathesis-based polymerization such as ring-opening metathesis polymerization (ROMP)<sup>[1]</sup> and ring closing metathesis (RCM)<sup>[2]</sup> reactions. The success of living polymerization by ROMP offers a new methodology for polymer synthesis. The RCM reaction of  $\alpha,\omega$ -diene offers cyclic compound by the intramolecular reaction of the  $\alpha,\omega$ -diene, which is competitive to the intermolecular reaction of the  $\alpha,\omega$ -diene. The intermolecular reaction of  $\alpha,\omega$ -diene catalyzed with Lewis acid free catalyst is called acyclic diene metathesis (ADMET) polymerization.<sup>[3,4]</sup> ADMET polymerization is a step growth, condensation polymerization that proceeds with metal carbene catalysts such as the Schrock catalyst containing molybdenum<sup>[5]</sup> or tungsten<sup>[6]</sup> and the Grubbs catalyst<sup>[4]</sup> containing ruthenium with acyclic diene. ADMET polymerization is a useful method for polymerizing various kinds of functionalized olefins to produce polymer that is perfectly linear and free from branching and other defects.<sup>[7-10]</sup> Because ethylene is a product of the reaction, the overall polymerization can be driven by the removal of ethylene from the system. In this polymerization, external diene polymerizes to give high molecular weight polymer, while monoolefin gives dimer. It is anticipated that ADMET polymerization of diene with monoolefin produces monoolefin terminated telechelic polymer which is a very useful intermediate material for the production of functional polymer<sup>[11-17]</sup> (Sch. 1).

Recently, we have demonstrated the synthesis of ester terminated telechelic polymers by ADMET polymerization of 1,9-decadiene with ester-containing monoolefins using Grubbs catalyst.<sup>[18]</sup> While the deprotection of ester moiety can be successfully achieved to give alcohol terminated telechelic polymer, this extra step must be done to give reactive telechelics.

Here, we report our recent results regarding the direct synthesis of reactive telechelic polymer containing epoxy functionality and its reactivity as the prepolymer for segmented copolymer.



Scheme 1. ADMET polymerization in several types.

## EXPERIMENTAL

### Materials

Grubbs' ruthenium catalyst was synthesized according to the literature method.<sup>[19]</sup> 1,9-Decadiene (**1**) and 1,2-epoxy-5-hexene (**3**) were purchased from Wako Pure Chemical Industries, Ltd. Other epoxy-containing monoolefins, 1,2-epoxy-4-pentene (**2**) and 1,2-epoxy-6-heptene (**4**), were synthesized by the conventional method.<sup>[20]</sup> The purified yields were 31% (**2**) and 56% (**4**), respectively. They were dried over calcium hydride and transferred into a round bottomed flask equipped with a high vacuum Teflon stopcock prior to use. All other chemicals were used without further purification.

### ADMET Polymerization

ADMET polymerization was performed under a reduced pressure at 90°C for 96 hr with a mole ratio of monomer/catalyst = 200/1. The ratio of diene/monoolefin was adjusted to 5/1. Ethylene as a by-product was removed every 3 hr from the reaction system, and the reaction was finished by exposing the reaction mixture to the air. The reaction mixture was dissolved in small quantity of chloroform, precipitated from acetone, and dried *in vacuo*. Optimal conditions for ADMET polymerization were determined by evaluating the molecular weight of the polymer as measured by gel permeation chromatography (GPC). Sampling of the reaction mixture (100  $\mu$ L) was done every 24 hr and this solution was diluted with THF and measured by GPC after passing through a 0.45  $\mu$ m membrane filter.

### Reaction of Telechelic Polymer with Diisocyanate

Epoxy terminated telechelic polymer was reacted with toluene diisocyanate in the presence of tributyl phosphate and lithium bromide in toluene at 90°C for 30 min.<sup>[21]</sup> The reaction mixture was precipitated from methanol, and dried *in vacuo*.

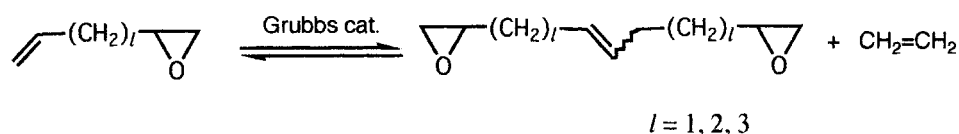
### Measurements

Proton NMR spectra were obtained with a JOEL JNM-EX270 superconducting spectrometer system. FT-IR spectra were measured with a Perkin Elmer PARAGON 1000 FT-IR spectrometer. 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<sub>HR</sub>, G3000H<sub>HR</sub> and G4000H<sub>HR</sub> columns.

## RESULTS AND DISCUSSION

## Dimerization of Epoxy-Containing Monoolefin

The reactivity of epoxy-containing monoolefins toward the Grubbs catalyst was elucidated by the dimerization reaction (Sch. 2). The epoxy-containing monoolefins (**2-4**) contained one to three methylene spacers between the olefin and the epoxy group. Each monoolefin was reacted with Grubbs catalyst at 80°C for 24 hr in the monoolefin/catalyst mole ratio of 200, and the resultant dimer was purified from the reaction mixture by silica gel column chromatography using chloroform as the eluent. Typical  $^1\text{H}$  NMR spectra of monoolefin (**3**) and its dimer are shown in Fig. 1, where disappearance of external olefinic peaks (5.0–5.1 ppm and 5.8 ppm) and appearance of internal olefinic peak (5.4 ppm) confirm the production of the



Scheme 2. Dimerization of epoxy-containing monoolefins.

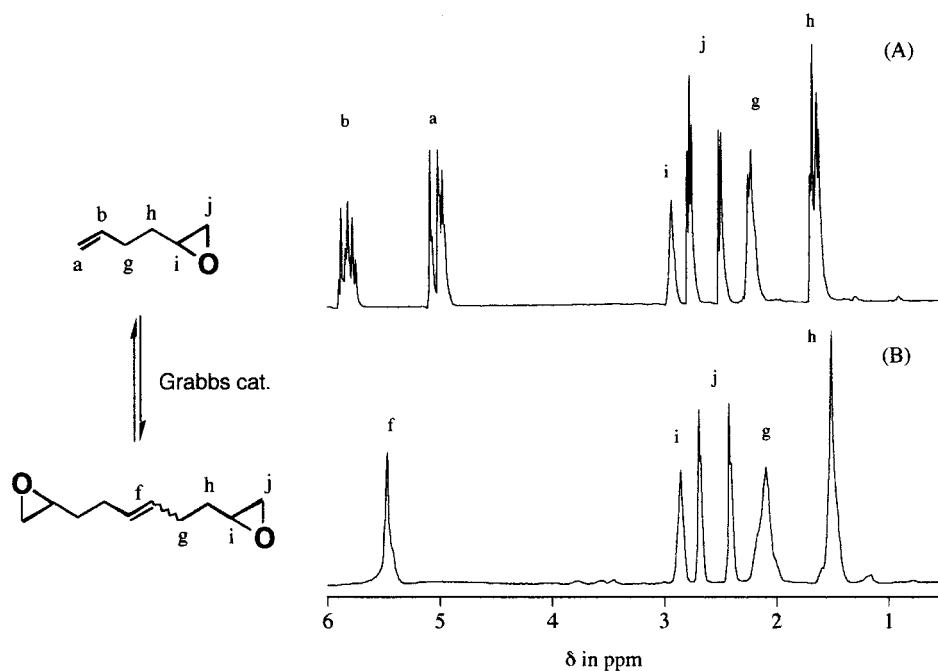


Figure 1.  $^1\text{H}$  NMR spectra of monoolefin (A) and dimer (B).

**Table 1.** Dimerization of Epoxy-Containing Monoolefin

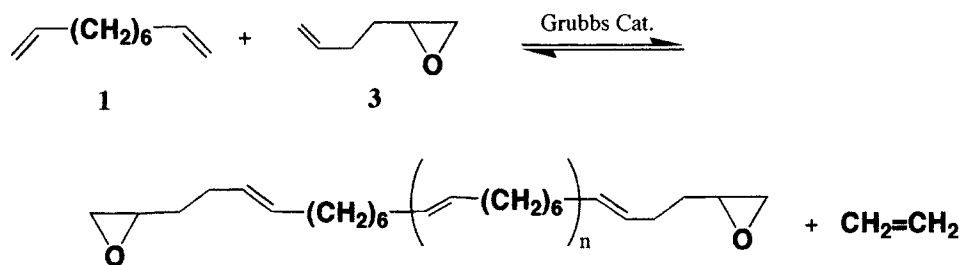
Monomer	<i>l</i>	Conversion <sup>a</sup> /%
2	1	44.5
3	2	90.9
4	3	98.6

<sup>a</sup>Monoolefin/catalyst = 200/1, diene/monoolefin = 5/1, Measured by <sup>1</sup>H NMR. Reaction time: 24 hr Temperature: 80°C.

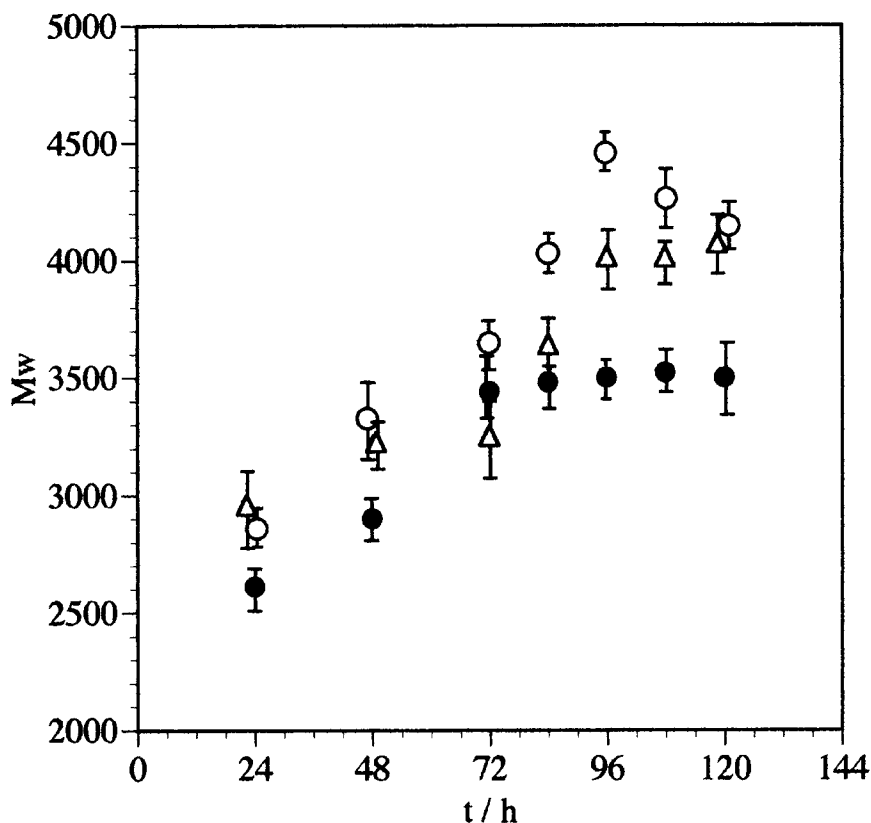
dimer. The conversion of the dimer was determined by the <sup>1</sup>H NMR analysis of reaction mixture, and the results are shown in Table 1. All the epoxy-containing monoolefins, even **2** with one methylene spacer, dimerized successfully using the ruthenium-based Grubbs catalyst. This observation is quite different from that found for ester-containing monomer catalyzed by molybdenum-based Schrock catalyst, where having less than two methylene spacers between the olefin and the ester moiety prevents polymerization.<sup>[7]</sup> Although molybdenum 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.<sup>[7]</sup> This phenomenon was minimized by the ruthenium catalyst demonstrated for the dimerization of epoxy-containing monoolefins (Table 1). The reactivity of the catalyst decreased with decrease of the number of methylene spacer. Nevertheless, the ruthenium catalyst is still active enough to drive dimerization even with one methylene spacer (**2**).

### Optimal Conditions for the ADMET Polymerization

Optimal conditions for the present ADMET polymerization were determined by combining of 1,9-decadiene (**1**) with 1,2-epoxy-5-hexene (**3**) in various ways (Sch. 3), where the molecular weight of the polymer served as an



**Scheme 3.** ADMET polymerization of 1,9-decadiene (**1**) with 1,2-epoxy-5-hexene (**3**).



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

index for making decisions. Molecular weights were measured by GPC in THF vs. polystyrene standards, using the reaction mixture without reprecipitation.

Effect of reaction temperature on molecular weight of the telechelic polymer is shown in Fig. 2. While the molecular weight of the polymers increased gradually with increased reaction time at 80 and 100°C, polymerization at 90°C reached a maximum molecular weight and decreased with time. The highest molecular weight (4450) was observed at 90°C after 96 hr. This is the same temperature as the polymerization of **1** with ester-containing monoolefin reported previously.<sup>[18]</sup>

Figure 3 shows the effect of monomer/catalyst ratio on molecular weight of the telechelic polymer examined at 90°C, where the ratio of diene/monoene was kept at 5/1. Molecular weight of the polymer approached the maximum value of 4450 after 96 hr in the case of 200/1, while those in 100/1 and 400/1 were less than in 200/1.

Thus, optimal condition for the present polymerization was determined to be monomer/catalyst ratio of 200/1 for 96 hr at 90°C. Reprecipitation of

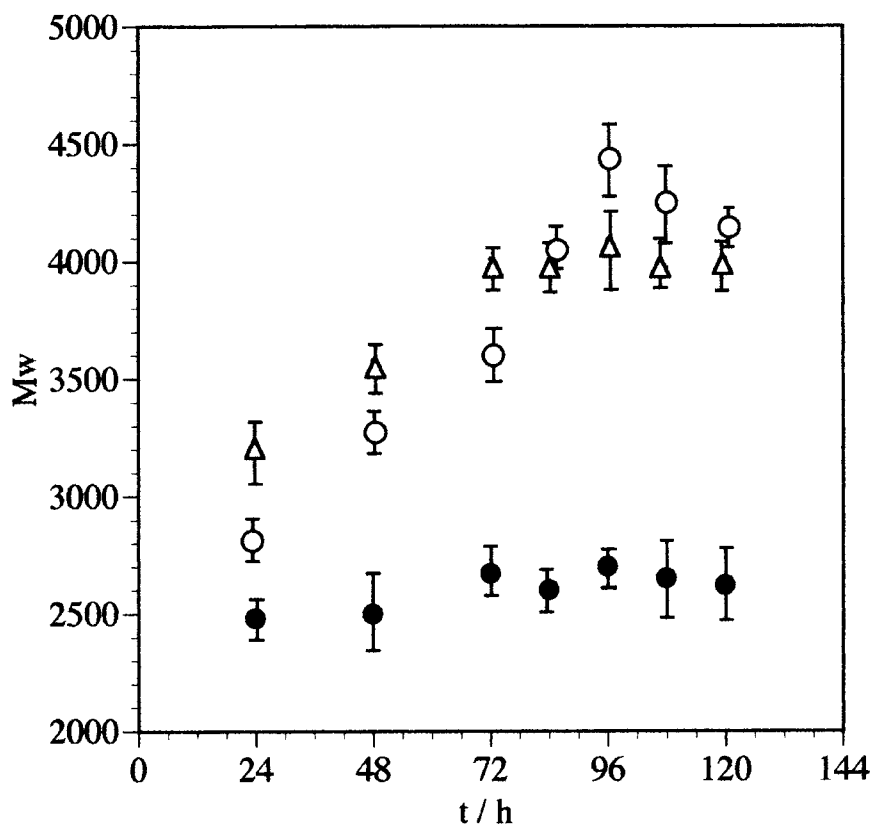


Figure 3. Effect of monomer/catalyst ratio on molecular weight of the telechelic polymer. ●: 100/1, ○: 200/1, △: 400/1.

the reaction mixture in chloroform/acetone synthesized under the optimal condition gave purified polymer of  $M_w = 7500$ ,  $M_n = 4700$  yielding a polydispersity of 1.96, similar to the theoretical value of 2, for step polymerization chemistry.

The results of the additional polymerizations for 1,9-decadiene (**1**) with epoxy-containing monoolefins (**2-4**) under optimal condition are shown in Table 2. All the epoxy-containing monoolefins, even **2** with one methylene spacer, polymerized successfully using the ruthenium catalyst. The molecular weight of the resultant telechelic polymer was a maximum when using **3** as the monoolefin. A stronger negative neighboring group effect might occur with shorter methylene spacer of epoxy-containing monoolefin. In this type of polymerization, epoxy-containing monoolefin acts as chain transfer agent<sup>[18]</sup> which controls the molecular weight. Molecular weight control was best observed using **4**, since this monoolefin has the highest reactivity of all the monoolefins to the Grubbs catalyst. Isolated yield of the polymers were low (15–35%), though the monomers are converted in high yield (83–93%).



**Table 2.** Effect of Chain Length of Epoxy-Containing Monoolefins on Molecular Weight of Telechelic Polymers

Monomer	<i>l</i>	Mn <sup>a</sup>	Mw <sup>a</sup>	Mw/Mn
2	1	4530	5810	1.32
3	2	4700	7500	1.96
4	3	2820	3760	1.33

<sup>a</sup>Monoolefin/catalyst = 200/1, diene/monoolefin = 5/1, determined by GPC (polystyrene standards), reaction time: 96 hr, temperature: 90°C.

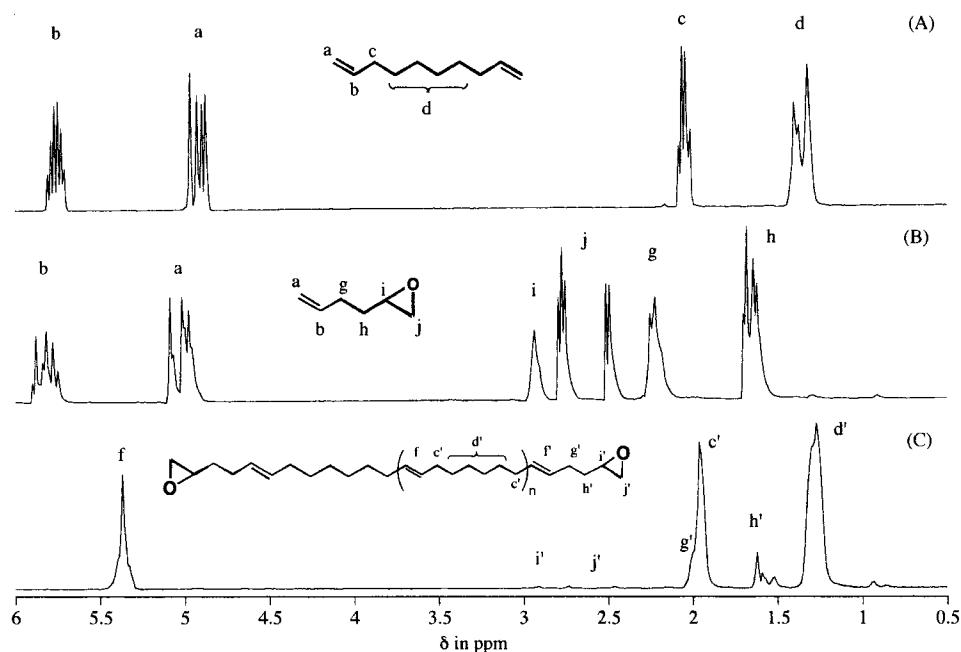
This observation most likely is due to polymer being lost in the reprecipitation procedure since molecular weights of the polymers are relatively low. It should be mentioned that ROMP chemistry can be used as well to produce telechelic oligomers.<sup>[14,15]</sup> The choice to do ADMET or ROMP is dictated by the availability of the monomers themselves.

### Structure of the Polymer

Figure 4 shows the <sup>1</sup>H NMR spectra of the epoxy terminated telechelic polymer synthesized under optimal condition and reprecipitated with chloroform/acetone (C), the monomer 1,9-decadiene (A) and the chain transfer agent 1,2-epoxy-5-hexene (B). The spectrum of the telechelic polymer (C) contains both poly(1,9-decadiene) (f, c', d') and epoxy (g'-j') components. Although the peak intensity attributed from h' is higher than the expected value, the peak area ratios contributed to poly(1,9-decadiene) and epoxy components are f : c' : d' = 1.0 : 1.8 : 3.9 and g' : i' : j' = 2.0 : 1.1 : 2.1, respectively, which are in good agreement with expected values. The spectrum contains a very strong internal olefinic peak (f; 5.3–5.4 ppm) and no external olefinic peaks (5 and 5.8 ppm from poly(1,9-decadiene)). These results strongly support the proposed structure of the epoxy terminated telechelic polymer.

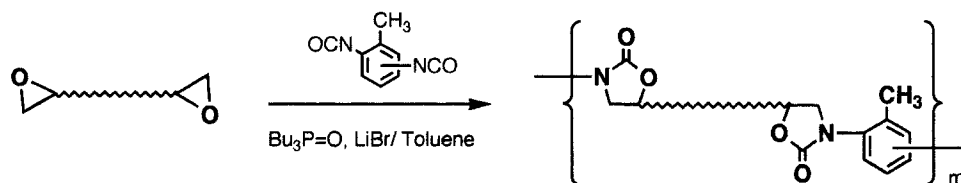
### Copolymerization of Telechelic Polymer

Reactivity and usefulness of the epoxy terminated telechelic polymer was elucidated via its reaction with toluene diisocyanate, where combining the epoxy and isocyanate functionalities produces oxazolidone moiety.<sup>[21]</sup> The subsequent polymerization is referred to as a forming a segmented copolymer. Optimal reaction condition was examined using styrene oxide and toluene diisocyanate as model compounds; both compounds were reacted in several solvents (toluene, xylene and benzene) at 80°C for 30 min in the presence of tributyl phosphate and lithium bromide as catalyst. The conversions were 60.0, 57.2, and 42.5%, respectively. The temperature de-



**Figure 4.** <sup>1</sup>H NMR spectra of 1,9-decadiene (A), 1,2-epoxy-5-hexene (B), and telechelic polymer (C).

pendence of this reaction was examined using toluene as the solvent, and it was found that the conversion was observed to be quantitative by raising the temperature up to 90°C. Consequently, the reaction of epoxy terminated telechelic polymer with toluene diisocyanate was performed at 90°C in toluene for 30 min (Sch. 4). The telechelic polymer (its GPC profile is shown in Fig. 5A) synthesized using **3** (with two methylene spacers) was used without further purification and reacted with toluene diisocyanate. Reaction mixture was reprecipitated with toluene/methanol giving purified polymer (42% yield) of  $M_w = 8000$  (Fig. 5B) in which peak separation procedure for the GPC peak profile of segmented copolymer (Fig. 5B) indicates the presence of two different polymer species.



**Scheme 4.** Synthesis of segmented copolymer with telechelic polymer and toluene diisocyanate.

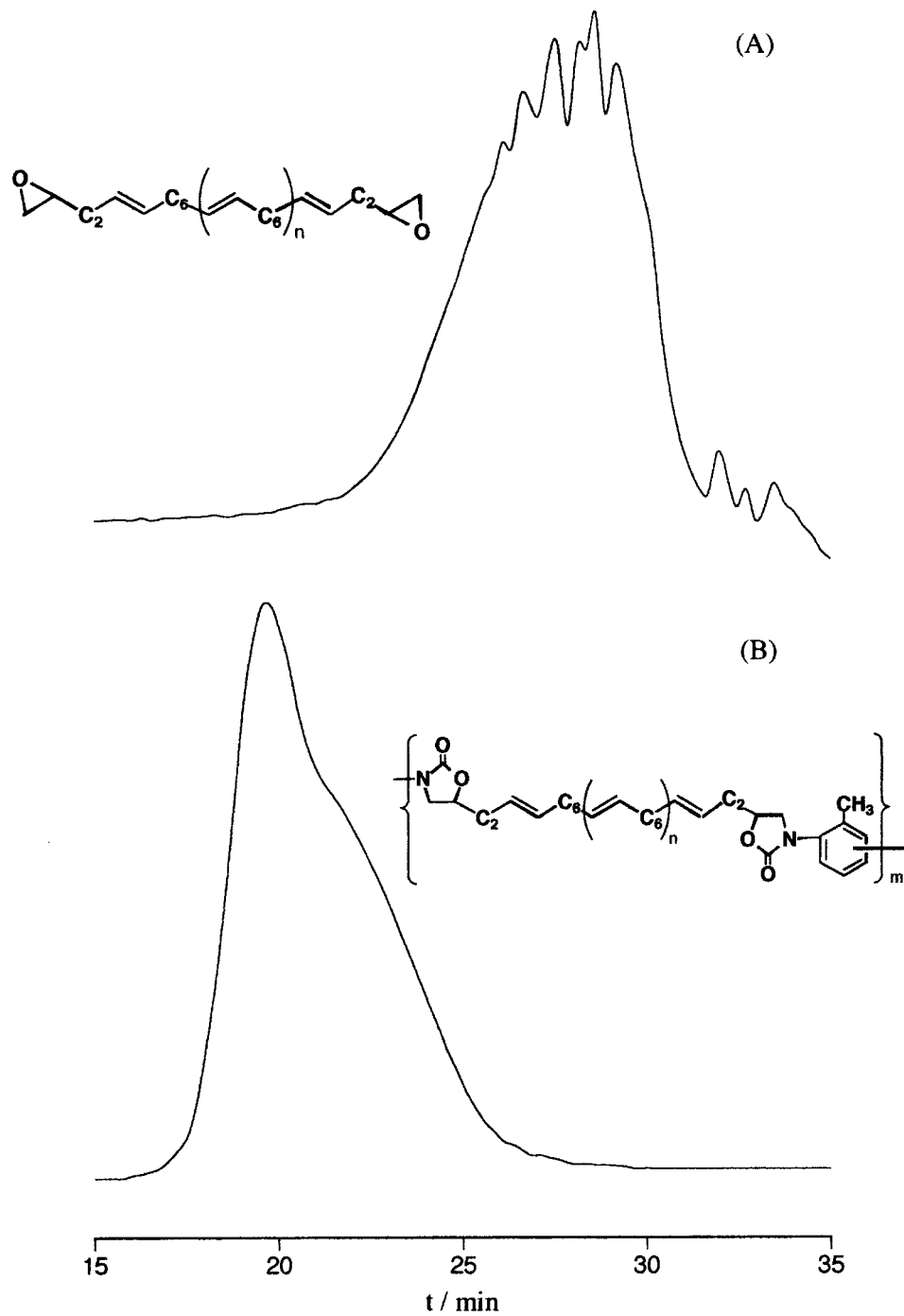


Figure 5. GPC traces of telechelic polymer (A) and segmented copolymer (B).

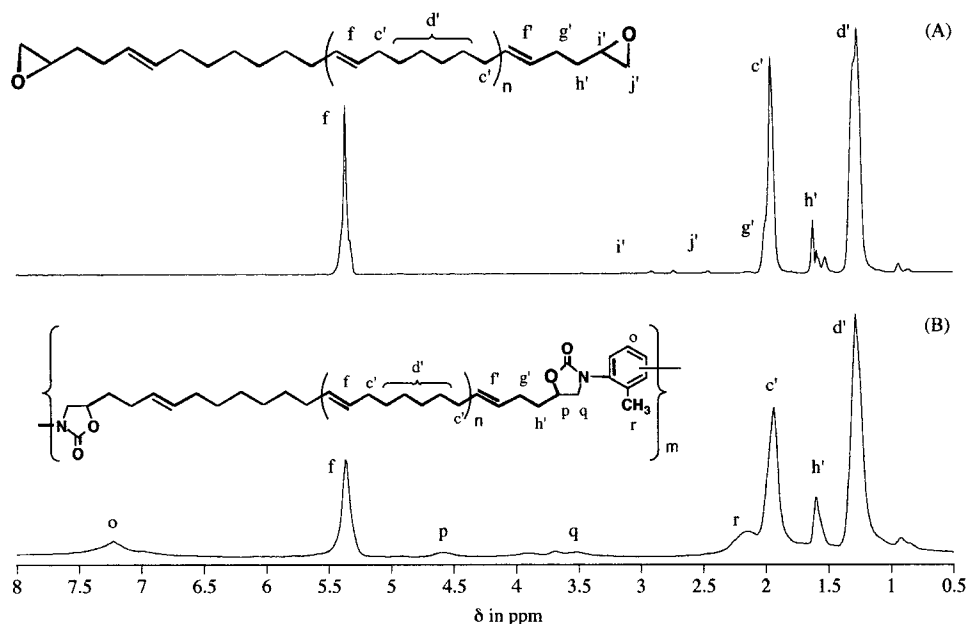


Figure 6. <sup>1</sup>H NMR spectra of telechelic polymer (A) and segmented copolymer (B).

Figure 6 shows the <sup>1</sup>H NMR spectra of epoxy terminated telechelic polymer (A) and segmented copolymer (B). The production of the desired segmented copolymer is supported by the disappearance of epoxy ring protons (i' and j') and the appearance of oxazolidone protons (p and q) and toluene protons (o and r). In addition, the proton signals attributed to poly(1,9-decadiene) moieties (c', d' and f) still appear in the segmented copolymer. Infrared spectroscopy shows a strong carbonyl stretching band around  $1730\text{ cm}^{-1}$  (Fig. 7). All these results strongly suggest that the present polymer is a segmented copolymer containing oxazolidone and poly(1,9-decadiene) moieties. However, two species of polymer structures suggested by the GPC measurement could not be examined by the present <sup>1</sup>H NMR and IR measurements. Separation and characterization of these two species are now underway.

Thus, the present epoxy terminated telechelic polymer is highly reactive with diisocyanate functional groups and is useful as a prepolymer. Presently the physical properties of the segmented copolymer are being examined, as are reactions of this epoxy terminated telechelic polymer with other difunctional compounds.

## CONCLUSION

ADMET polymerization of 1,9-decadiene with epoxy-containing monoolefins with various numbers of methylene spacers between the olefin

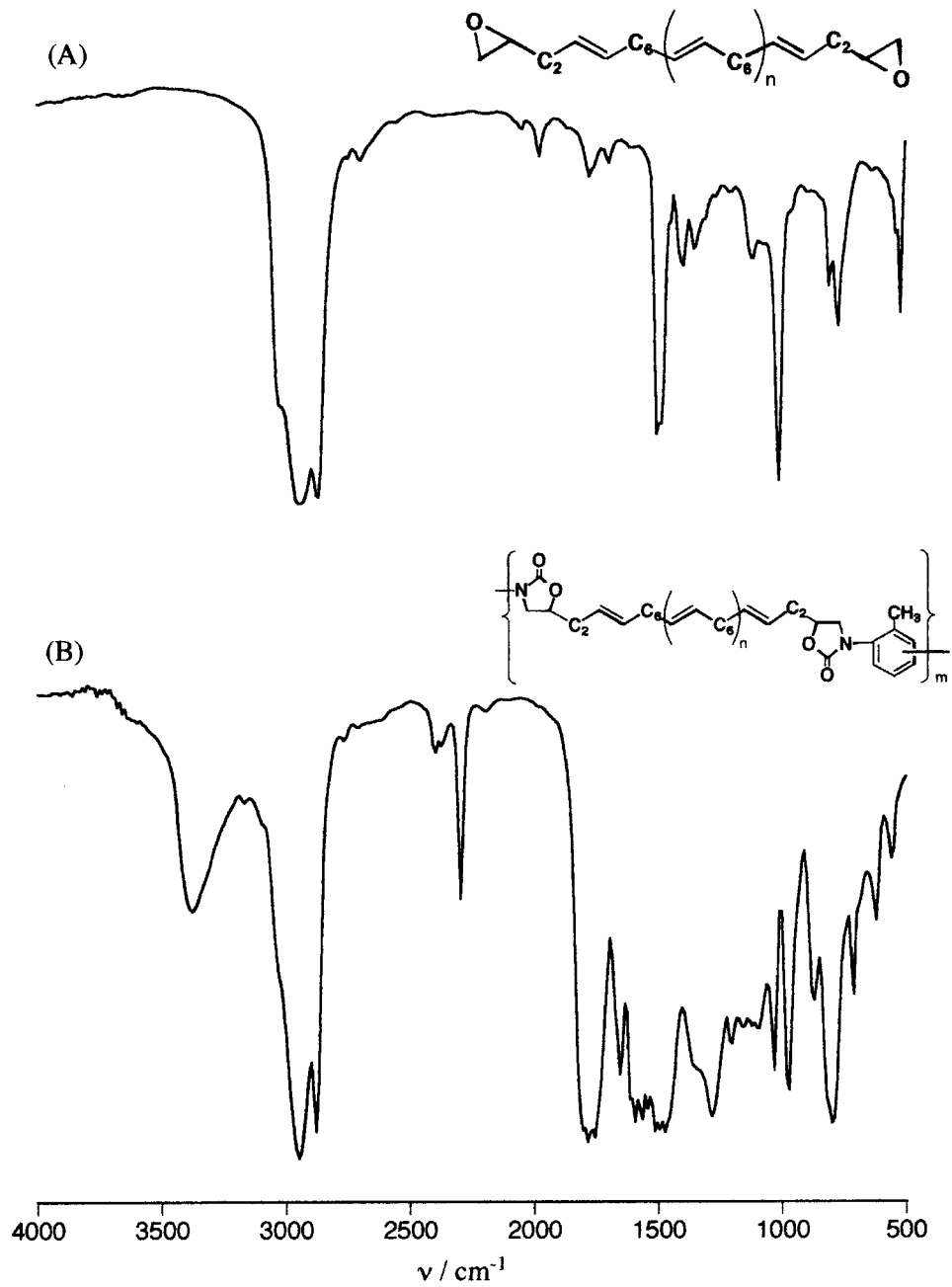


Figure 7. IR spectra of telechelic polymer (A) and segmented copolymer (B).

and the epoxy using ruthenium based Grubbs catalyst was successfully achieved to give epoxy terminated telechelic polymers. The optimal condition of the present ADMET polymerization was determined as monomer/catalyst ratio of 200/1 for 96 hr at 90°C, which gave the polymer with weight-average molecular weight of 7500. Due to negative neighboring group effect and the chain transfer nature of epoxy-containing monoolefin, the molecular weights of the telechelic polymers depend on the number of methylene spacer of the epoxy-containing monoolefins. The reaction of terminal epoxy group of telechelic polymer with diisocyanate successfully gave higher molecular weight segmented copolymer connected with oxazolidone linkage.

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