Synthesis and Thermal Properties of Enyne-Containing Polymers by the Polymerization of Diynes Using a Low-Valent Titanium Catalyst

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Summary

Polymers having conjugated enyne moieties in the main chain (**3**) were prepared by the polymerization of diynes (**2**) using a low-valent titanocene catalyst (**1**) generated from $Cp^*_2TiCl_2$ and i-PrMgBr. The reactivity of the enyne-containing polymers (**3**) was demonstrated by the thermal cross-linking reaction at 200 °C.

Introduction

Conjugated enyne moieties are attractive building blocks to be incorporated into polymers because of their unique reactivity and potential functions [1]. Previously, the synthesis of polymers containing conjugated enyne unit in the main chain was performed by the Pd-catalyzed polymerization of bis(2-bromoethenyl)benzenes and diethynylbenzene derivatives [2]. We also described a novel synthetic method of the enyne-containing polymers by the Pd-catalyzed three-component coupling polymerization of norbornadiene, aryl dihalides, and bis(organotin)s and the subsequent retro Diels-Alder reaction [3]. The enyne-containing polymers with arylene linkages thus obtained exhibit strong photoluminescence, indicating the potential application of the polymers as optoelectronics materials. Based on the reactivity of enyne moieties in the polymers, it is also possible to prepare novel reactive polymers, and crosslinkable materials. In spite of these potential applications, the synthetic methods for the enyne-containing polymers are limited to the above mentioned coupling processes. Because enyne derivatives can be prepared by the dimerization of terminal acetylenes, the polymerization using the dimerization process might serve as an alternative promising method for enyne-containing polymers. Among many dimerization reactions reported, the Cp^*_2Ti-catalyzed one reported by Akita et al. [4] is an attractive method because this reaction proceeds under mild conditions giving rise to enynes in a regiospecific fashion.

Accordingly, we describe herein the polymerization of diynes by means of the catalytic dimerization of terminal acetylenes using a low-valent titanium complex. In order to demonstrate the reactivity of the polymers, the thermal cross-linking behavior of the obtained polymers was also studied.

Experimental

Materials and instruments

Bis(pentamethycyclopentadienyl)titanium dichloride (Cp*$_2$TiCl$_2$) was prepared according to the literature [5]. 1,7-Octadiyne (**2a**) and 1-hexyne (**4a**) were distilled and stored under argon. 1,4-Bis(2-propynyloxy)benzene (**2b**) and phenyl propargyl ether (**4b**) were obtained as described or with slight modification [6]. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen. Nuclear magnetic resonance (NMR) spectra were measured on a using JEOL JNM ECP300 instrument using tetramethylsilane as an internal standard (300 MHz and 75 MHz for ^{1}H and ^{13}C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS equipped with Tosoh TSK-gel GMH$_{HR}$-M tandem columns using chloroform as an eluent at 35 °C. Polystyrene standards were used for calibration. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 instrument. Differential scanning calorimetric (DSC) measurements were carried out on a Shimadzu DSC-60 instrument. TGA and DSC measurements were performed under nitrogen at a scan rate of 10 °C/min.

Model Reactions (Typical Procedure for 5a)

The model compound (**5a**) was prepared according to the reported method [7]. To a solution of Cp*$_2$TiCl$_2$ (16 µg, 40 µmol) in THF (1.0 ml) was added a diethyl ether solution of *i*-PrMgBr (1.00 M, 240 µl, 2.40 µmol) at ambient temperature and the mixture was stirred for 10 min. To the resulting mixture was added **4a** (0.164 g, 2.00 mmol) at 0 °C and the mixture was stirred at 30 °C for 12 h. After the addition of aqueous hydrochloric acid (3.00 N ca. 1 ml), the resulting mixture was poured into water (10 ml). The organic layer was collected and the remaining aqueous phase was extracted three times with hexane. After drying over MgSO$_4$ and concentration, purification of the products was performed by a silica gel column chromatography (eluent: hexane) to give **5a** in 95 % yield (0.156 g, 1.90 mmol) as a colorless oil.

5a: ^{1}H NMR (δ, CDCl$_3$) 0.86 (m, -C*H*$_3$, 6H), 1.19-1.47 (m, -CH$_2$C*H*$_2$C*H*$_2$CH$_3$, 8H), 2.05 (t, *J* = 7.5 Hz, -C*H*$_2$-C=, 2H), 2.26 (t, *J* = 6.6 Hz, -C*H*$_2$-C≡, 2H), 5.04 (s, C=C*H*$_2$, 1H), 5.12 (s, C=C*H*$_2$, 1H) ppm; ^{13}C NMR (δ, CDCl$_3$) 13.6 (-*C*H$_3$), 13.9 (-*C*H$_3$), 19.0 (-*C*H$_2$-C≡), 22.0 (-*C*H$_2$CH$_3$), 37.3 (-*C*H$_2$-C=), 81.0 (-*C*≡C-C=), 90.0 (-C≡*C*-C=), 119.3 (-*C*=CH$_2$), 132.4 (-C=*C*H$_2$) ppm; IR (NaCl, neat) 3091, 2962, 2956, 2880, 2856, 2771, 2235, 1660, 1642, 1453, 1395, 1333, 1117, 892 cm^{-1}.

5b: 80 % yield; ^{1}H NMR (δ, CDCl$_3$) 4.48 (s, -C*H*$_2$-C=, 2H), 4.78 (s, -C*H*$_2$-C≡, 2H), 5.58 (s, C=C*H*$_2$, 1H), 5.63 (s, C=C*H*$_2$, 1H), 6.92 (m, C$_6$H$_5$, 6H), 7.25 (m, C$_6$H$_5$, 4H) ppm; ^{13}C NMR (δ, CDCl$_3$) 56.3 (-O-*C*H$_2$-C≡), 69.2 (-O-*C*H$_2$-C=), 84.7 (-*C*≡C-C=), 85.5 (-C≡*C*-C=), 114.9, 115.0, 121.1, 121.4, 123.4, 126.3, 129.4, 157.6, 158.1 (-*C*=CH$_2$, -C=*C*H$_2$, -*C*$_6$H$_4$-) ppm; IR (NaCl, neat) 3063, 3040, 2920, 2863, 2227, 1932, 1846, 1701, 1599, 1494, 1456, 1373, 1336, 1304, 1238, 1215, 1172, 1080, 1032, 1010, 993, 916, 883, 835 cm^{-1}.

Polymerizations (Typical Procedure for 3a)

To a solution of Cp*$_2$TiCl$_2$ (16 µg, 40 µmol) in THF (1.0 ml) was added a diethyl ether solution of *i*-PrMgBr (1.00 M, 240 µl, 2.40 µmol) at ambient temperature and the mixture was stirred for 10 min. To the resulting mixture was added **2a** (0.210 g,

2.00 mmol) at 0 °C and the mixture was stirred at 30 °C for 24 h. After the addition of aqueous hydrochloric acid (3.00 N, ca. 1 ml), the organic layer was concentrated and precipitated into methanol to give **3a** in 84 % yield (0.177 g, 1.67 mmol unit) as a yellow powder. A polymer (**3b**) was prepared under similar conditions.

3a: ^{1}H NMR (δ, CDCl$_3$) 1.4-1.6 (m, -CH$_2$CH_2CH_2CH$_2$-, 4H), 2.00 (m, -CH_2-C=, 2H), 2.31 (m, -CH_2-C≡, 2H), 5.01 (m, C=CH_2, 1H), 5.19 (m, C=CH_2, 1H) ppm; ^{13}C NMR (δ, CDCl$_3$) 18.9 (-CH$_2$-C≡), 27.5 (-CH$_2$$CH_2$$CH_2$$CH_2$-), 37.0 (-$CH_2$-C=), 81.2 (-$C$≡$C$-C=), 89.7 (-C≡$C$-C=), 119.6 (-$C$=CH$_2$), 131.9 (-C=$CH_2$) ppm; IR (NaCl, film) 3092, 2937, 2216, 1610, 1433, 1331, 1261, 1091, 1022, 893, 802 cm^{-1}.

3b: Yield 72 %; ^{1}H NMR (δ, CDCl$_3$) 4.44 (m, -O-CH_2-C=, 2H), 4.75 (m, -O-CH_2-C≡, 2H), 5.58 (m, C=CH_2, 1H), 5.63 (m, C=CH_2, 1H), 6.82 (m, -C$_6$$H_4$-, 2H), 6.89 (m, -C$_6$$H_4$-, 2H) ppm; ^{13}C NMR ($\delta$, CDCl$_3$) 57.2 (-O-$CH_2$-C≡), 70.1 (-O-$CH_2$-C=), 84.7 (-$C$≡C-C=), 85.6 (-C≡$C$-C=), 116.0 (-$C_6H_4$-), 123.3 (-$C$=CH$_2$), 126.5 (-C=$CH_2$), 152.6 (-$C_6H_4$-) ppm; IR (NaCl, film) 3036, 2968, 2932, 2870, 2226, 1890, 1609, 1582, 1510, 1456, 1365, 1298, 1222, 1182, 1107, 1068, 1012, 912, 829 cm^{-1}.

Results and Discussion

On the basis of the catalytic dimerization of terminal acetylenes by a low-valent titanium complex (**1**) generated from Cp*$_2$TiCl$_2$ and i-PrMgBr [4], the polymerization of diynes (**2a** and **2b**) was carried out in the presence of **1** (2 mol%) in THF at 30 °C for 24 h under argon atmosphere (Scheme 1 and Table 1). For example, a yellow powdery polymer (**3a**) having conjugated enyne moieties in the main chain was obtained in 84 % yield, which is soluble in common organic solvents such as THF, CHCl$_3$, and toluene [8]. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of **3a** were estimated as 21,000 and 2.0, respectively (run 1).
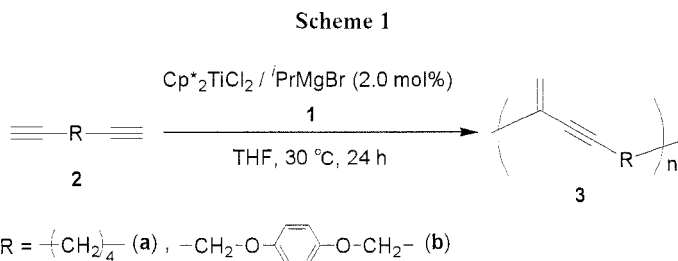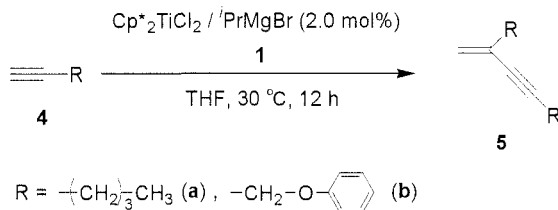
Scheme 1

$$R = -(CH_2)_4- \ (a), \ -CH_2-O-\langle\!\langle\!\rangle\!\rangle-O-CH_2- \ (b)$$

Table 1. Synthesis of polymers (**3**) having enyne moieties in the main chain.

Run	Polymer	Yield (%)^a	$M_n^{\ b}$	$M_w/M_n^{\ b}$
1	**3a**	84	21,000	2.0
2	**3b**	72	1,800	2.5

^{a} MeOH-insoluble part. ^{b} Estimated by GPC (CHCl$_3$, polystyrene Std).

In the case of a bis(propargyl ether) (**2b**), a polymer (**3b**) with relatively lower molecular weight was produced. The insufficient polymerizability of **2b** might be due to the presence of the oxygen atom in the diyne monomer. In fact, the model reactions of monofunctional terminal acetylenes (**4a** and **4b**) carried out in the presence of **1** gave rise to enynes (**5a** and **5b**, respectively) where the yield of **5b** (80 %) was lower than that of **5a** (95 %) (Scheme 2).

Scheme 2

$Cp^*_2TiCl_2 / {}^iPrMgBr$ (2.0 mol%)

1

THF, 30 °C, 12 h

4 $\quad\longrightarrow\quad$ **5**

$R = -(CH_2)_3CH_3$ **(a)** , $-CH_2-O-\langle\!\!\langle\ \rangle\!\!\rangle$ **(b)**

The structural elucidation of the polymers (**3a** and **3b**) was performed by the ^{1}H NMR, ^{13}C NMR and IR spectra in comparison with those of the corresponding model compounds (**5a** and **5b**). The ^{1}H NMR spectrum of the enyne (**5a**) exhibited peaks attributable to the aliphatic protons and the olefinic protons in the exo-methylene moieties at 0.9-2.3 ppm and 5.0-5.1 ppm, respectively (Figure 1a). In accordance with this spectrum, the corresponding peaks (i.e. aliphatic methylenes and olefinic protons) are observed in that of the polymer (**3a**) (Figure 1b). The integral ratio of these two peaks (8.0:2.0) is in good accordance with the ratio for the expected structure. In the ^{13}C NMR spectrum of **3a**, peaks attributable to the triple bond moieties in the main chain are also observable at 81 ppm and 90 ppm. The presence of a peak at 2216 cm^{-1} in the IR spectrum also supports that the polymer (**3a**) contains the triple bond moieties.
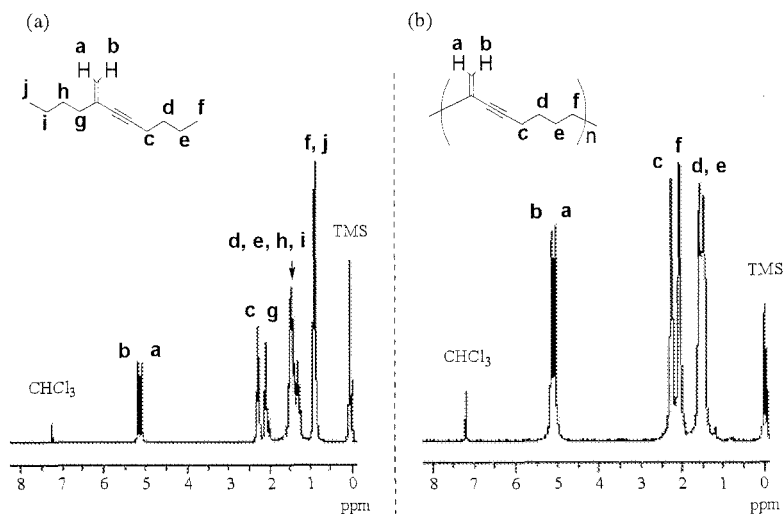

Figure 1. ^{1}H NMR spectra of **5a** (a) and **3a** (b).

Reflecting upon the reactivity of the enyne moieties, the polymers are potentially applicable as novel reactive materials. For example, the excellent thermal cross-linking ability of the polymers could be demonstrated by the following experiment. On heating the powdery polymer (**3a**) at 200 °C in a degassed sealed tube for 1 h, the polymer became completely insoluble in organic solvents. The thermogravimetric analysis (TGA) of **3a** revealed that no weight loss occurred below 200 °C. In the

differential scanning calorimetric (DSC) analysis of **3a** (measured under nitrogen, at a scan rate of 10 °C/min), an exothermic peak was observed whose onset and peak top temperatures are approximately 80 °C and 157 °C, respectively (Figure 2). Since the corresponding exothermic peak was not observable in the second heating cycle of the DSC measurement, irreversible chemical reactions (i.e., the cross-linking reactions) most probably take place on heating the enyne-containing polymer. In the IR spectrum of the polymer after heating at 200 °C, the peak at 2216 cm^{-1} attributable to the C≡C stretching vibration almost disappeared, suggesting that the reactions at the triple bond moieties are involved in the cross-linking process (Figure 3). This result suggests that the polymer (**3a**) is potentially applicable as a novel curing system consisting of pure hydrocarbon unit.
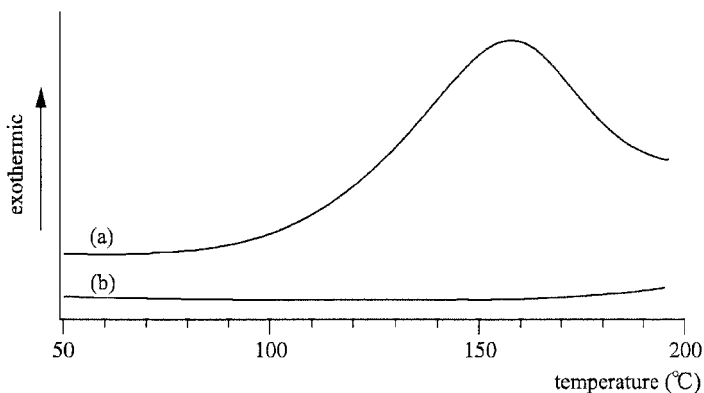

Figure 2. DSC thermogram of **3a** taken at the first (a) and the second (b) heating cycles (under N$_2$, scan rate; 10 °C/min).
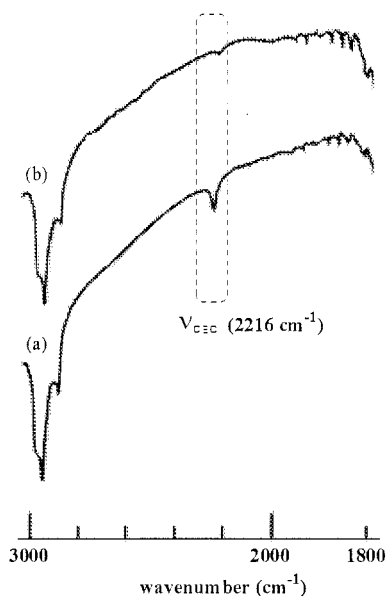

Figure 3. IR spectra of **3a** (KBr disk) before (a) and after (b) curing at 200 °C for 1 h.

In summary, polymers having enyne moieties in the main chain were prepared by the polymerization of diynes using a low-valent titanium catalyst. The resulting polymers were found to undergo thermal cross-linking reaction to give insoluble materials. Further studies on the polymerization of diynes and applications of the resulting polymers are in progress.

References and Notes

1. (a) Burrell RC, Daoust KJ, Bradley AZ, DiRico KJ, Johnson RP (1996) J Am Chem Soc 118: 4218 (b) Gevorgyan V, Takeda A, Homma M, Sadayori N, Radhakrishnan U, Yamamoto Y (1999) J Am Chem Soc 121: 6391
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6. Whitlock BJ, Whitlock HW Jr (1983) J Am Chem Soc 105: 838
7. In ref. (4), the enyne derivative (5a) was obtained in an almost comparable yield (91%).
8. Within the examined conditions, this catalyst seems not to be suitable for the polymerization of aromatic diynes such as 1,4-diethynylbenzene and its derivatives. For example, the reaction of 1,4-diethynylbenzene gave rise to oligomers as a result of the insufficient conversion of acetylene moieties, while 2,5-dialkoxy-1,4-diethynylbenzenes provided insoluble crosslinked products by means of the cyclotrimerization of the acetylene moieties.