

이중결합을 가지는 5원환 고리화합물의 합성 및 중합 Synthesis, Design and Polymerization of 5-membered exo methylene Cyclic Acetals

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〈요 약〉

5원환 고리아세탈 화합물인 4-methylenes(4,5)을 합성하고 저온조건 하에서 중합반응을 조사한 결과, 선택적인 개환중합이 일어났다. 보통의 양이온 개시제를 사용한 결과 -78°C 에서 가교체가 얻어졌으며, $\text{CH}_3\text{SO}_3\text{H}$ 를 개시제로 사용하면 같은 조건에서도 주사슬과 곁사슬에 이중결합을 가지는 개환중합체가 얻어진다. 이 중합체는 반응성을 가지는 불포화기를 포함하고 있으므로 prepolymer로써 널리 사용될 수 있다.

Keywords: selective polymerization, 5-membered exo methylene acetal, keto-ether, crosslinked polymer, alkenyl group

1. Introduction

A lot of attention has been made to develop functional polymers with reactive or polymerizable functional groups such as epoxy and acrylate groups. One approach to these polymers is the polymerization of monomers with dual polymerizable groups, which are different in structure and undergo polymerization with different mechanism. Selective polymerization of monomers with two polymerizable carbon-carbon double bonds seems to be useful to synthesize functional polymers containing double bonds. However, from a synthetic point of view, monomers with two similar polymerizable groups can be easily prepared in contrast to those with two

different polymerizable groups although the two similar polymerizable groups in the monomer are liable to polymerize simultaneously to give cross-linked insoluble polymer.

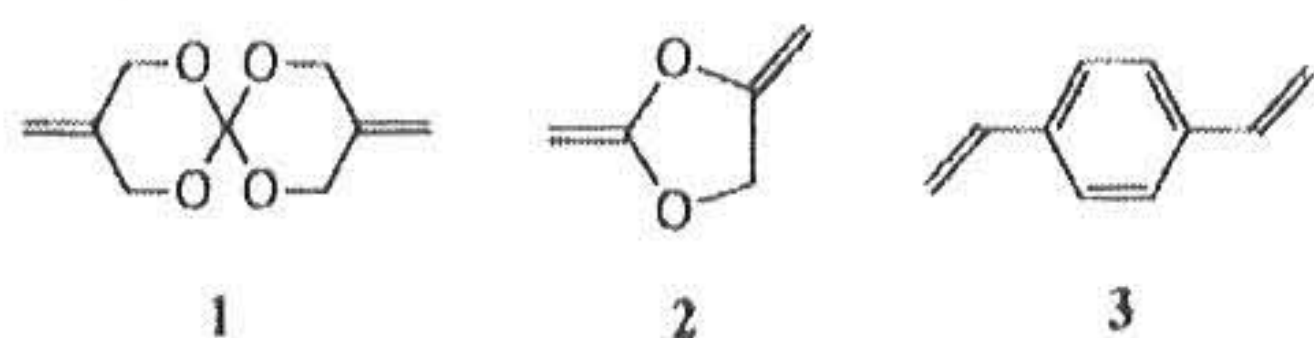
In previous articles, we have reported successful results of selective polymerization of monomers 1~3 with two polymerizable carbon-carbon double bonds as shown in figure 1. It can make some functional polymers with carbon-carbon double bond in the side chain. Thus, cyclic monomers 1¹ and 2² undergo radical ring-opening polymerization to obtain poly (ether-carbonate) and polyester with carbon-carbon double bond in the side chain, respectively. Tsuruta and Nagasaki have reported successful result of selective anionic polymerization of

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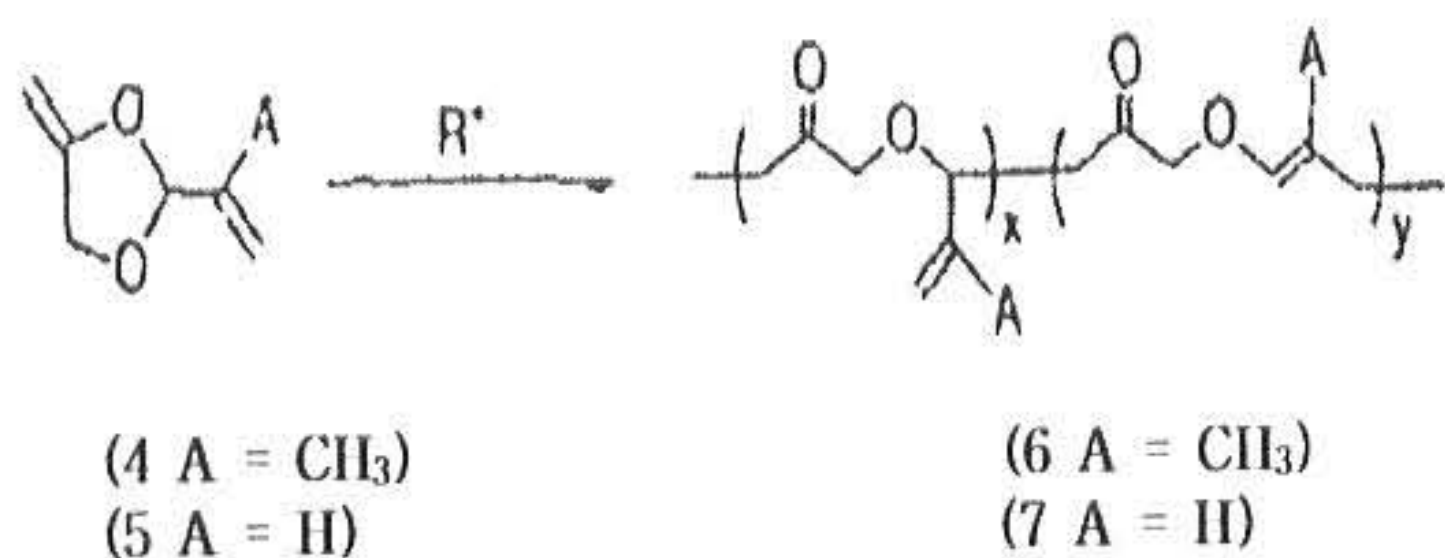
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divinylbenzene 3³.

(Figure 1)



This article involves extensive work to the cationic polymerization of new 5-membered exo methylene cyclic acetals 4, 5 having two carbon-carbon double bonds, which affords selective poly (keto-ether) containing the alkenyl group and vinyl ether skeletons under cationic polymerization conditions by virtue of



ring-opening polymerization. Although radical⁴ and cationic polymerization⁵ of 5-membered cyclic acetals with one carbon-carbon double bond have been reported, there are few examples of polymerization for the 5-membered cyclic acetals with two carbon-carbon double bonds except for our report on the radical polymerization of 2⁶.

2. Experimental

A solution of 76g (1.1mol) of methacrolein and 94.5g (1mol) of epichlorohydrin in 250mL of benzene was stirred at room temperature, and 1.4g of stannic chloride in 20mL of benzene was added with stirring. After the reaction solution was held at 25°C for 1.5h, 0.7g of stannic chloride in 10mL of benzene was added to the mixture, and the mixture was allowed to stand overnight. Five grams of calcium oxide was added with stirring before the benzene and excess methacrolein was removed at reduced pressure. The residue was distilled. 84.6g (yield 52%) bp

70-72°C/10mmHg.

A solution of 81.3g (0.5mol) of 2-isopropenyl-4-chloromethyl-1,3-dioxolane and 108g (1mol) of sodium methoxide in 65mL of DMF was stirred at room temperature overnight. The reaction mixture was poured into water and extracted with ether. Ether was removed from the organic layer at reduced pressure before distillation. 46.4g (yield 73%) bp 80-82°C/100mmHg

Cationic Polymerization of 4 : In the three-neck flask fitted with a nitrogen gas inlet and outlet, 0.5g (4mmol) of 4 and 8mL of dry dichloromethane were placed. After cationic catalyst (2mol%) was added, the mixture was stirred at -78°C. The reaction mixture was quenched with alcoholic NH₃ solution. Monomer conversion was determined by gas chromatography. The quenched reaction mixture was washed with 27% aqueous sodium bicarbonate solution and then with water to remove initiator residues and evaporated to dryness under reduced pressure to give only polymer. It was dissolved in dichloromethane and the solution was poured into a large amount of *n*-hexane to precipitate the polymers. After the hexane layer was removed by decantation, the isolated polymer was dried under vacuum. The hexane layer was evaporated to give the hexane-soluble polymer. The obtained polymer was confirmed by IR and NMR. A solution of 61.8g (1.1mol) of acrolein and 94.5g (1mol) of epichlorohydrin in 250mL of benzene was stirred at room temperature, and 1.4g of stannic chloride in 20mL of benzene was added with stirring. A solution of 28.1g (0.5mol) of 4-chloromethyl-1,3-dioxolane and 108g (1mol) of sodium methoxide in 65mL of DMF was stirred at room temperature overnight. Following was same as that of 2-isopropenyl-4-methylene-1,3-dioxolanes. 60.1g (yield 52%) bp 32-33°C/15mmHg

Cationic Polymerization of 5 : In the three-neck flask fitted with a nitrogen gas inlet and outlet, 0.46g (4mmol) of 5 and 8mL of dry dichloromethane were placed. Following was same method of 4.

Measurement : ^1H - and ^{13}C -NMR spectra were recorded on JEOL JNM-EX400 and JNM-EX90 spectrometers (90 MHz for ^1H - and 100 MHz for ^{13}C -NMR), using tetramethylsilane (TMS) as an internal standard in deuteriochloroform (CDCl_3) at 27°C . IR spectra were obtained with JASCO FT/IR-5300 spectrometer at 27°C . Molecular weights and the distribution were estimated by gel permeation chromatography (GPC) on Tosoh HPLC CCP & 8000 system with data processor.

3. Results and Discussion

2-Isopropenyl-4-methylene-1,3-dioxolane(4) was prepared from methacrolein and epichlorohydrin in two steps as shown in scheme 2. Acetalization of methacrolein and epichlorohydrin was performed in the presence of tin(IV) chloride in benzene at room temperature to obtain 2-isopropenyl-4-chloromethyl-1,3-dioxolane in 52% yield according to a reported procedure of similar acetalization⁷. Dehydrochlorination of the chloromethylated dioxolane with sodium methoxide was performed in DMF at ambient temperature to give the desired cyclic acetal 4 containing two carbon-carbon double bonds, which were stable toward water, compared to cyclic acetals 2-methylene-1,3-dioxolanes.

Table 1. Cationic Polymerization of 4^a

Run	Catalyst(Mol%)	Time (h)	Yield ^b %	M_n^c	x and y in the polymer (mol%) ^d	mole ratio ^e x : y
1	BF_3OEt_2 (2)	1	60 ^f	--	--	--
2	$\text{CF}_3\text{SO}_3\text{H}$ (2)	1	70 ^f	--	--	--
3	$\text{CH}_3\text{SO}_3\text{H}$ (2)	0.5	72	2000	87	70 : 30
4	$\text{CH}_3\text{SO}_3\text{H}$ (2)	1.5	88	4500	56	70 : 30
5	$\text{CH}_3\text{SO}_3\text{H}$ (0.5)	22	60	2500	79	70 : 30
6	$\text{CH}_3\text{SO}_3\text{H}$ (1)	1	70	3000	84	70 : 30
7	$\text{CH}_3\text{SO}_3\text{H}$ (1)	8	86	5000	62	74 : 26

^a Polymerization was carried out in dichloromethane at -78°

^b Insoluble in *n*-hexane

^c By GPC calibrated with standard polystyrene

^d Estimated by ^1H -NMR using benzene as an internal standard

^e Estimated by ^1H -NMR

^f Crosslinked polymer.

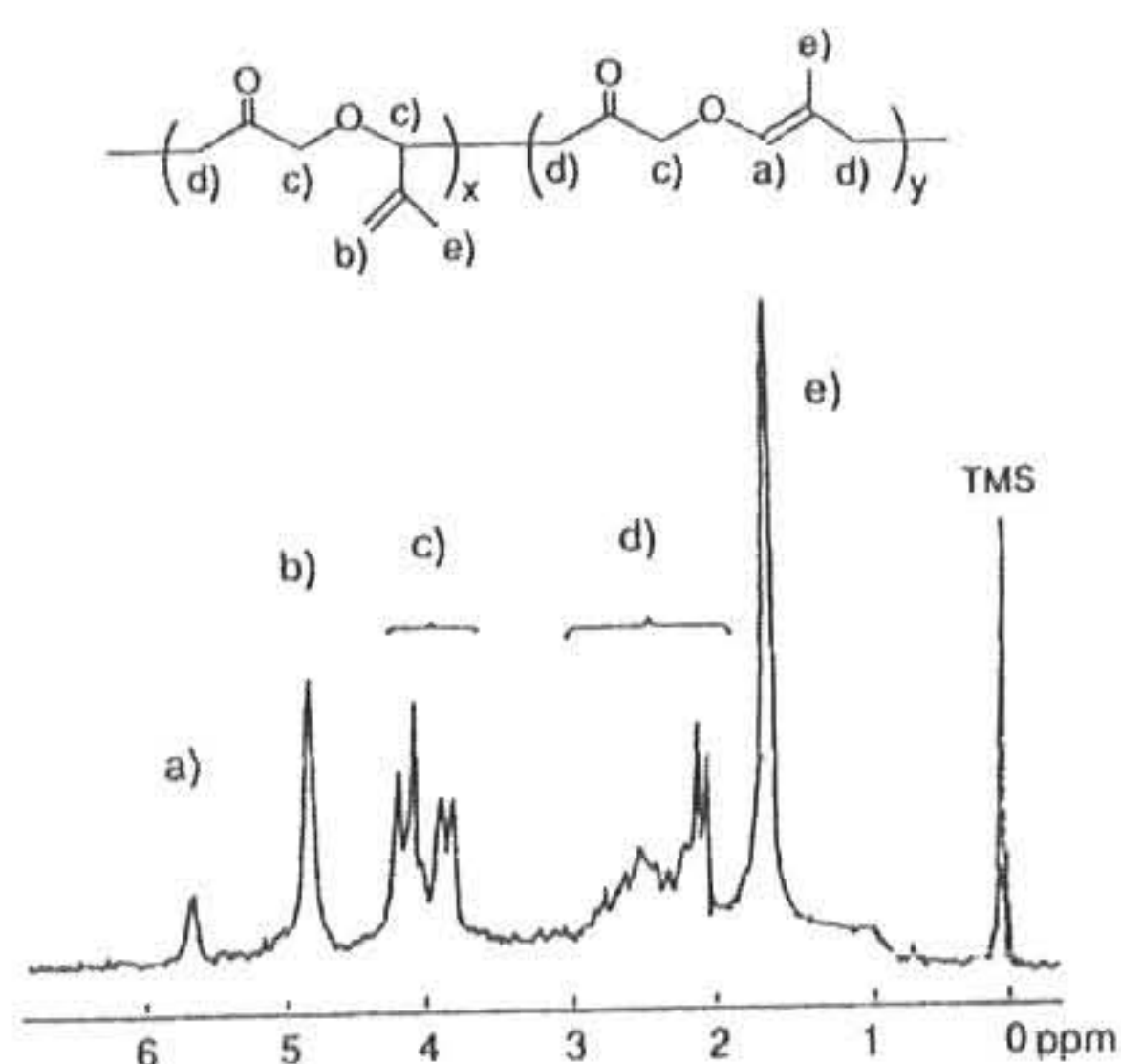


Figure 2. ^1H -NMR spectra of polymer (run 3, Table 1)

Cationic Polymerization of 4 : Cationic polymerization of 4 was performed in dichloromethane with BF_3OEt_2 , $\text{CF}_3\text{SO}_3\text{H}$, and $\text{CH}_3\text{SO}_3\text{H}$ as cationic catalysts. The results are summarized in Table 1. Only crosslinked polymers were obtained even at -78°C with BF_3OEt_2 and $\text{CF}_3\text{SO}_3\text{H}$, whereas soluble polymers were obtained with $\text{CH}_3\text{SO}_3\text{H}$ in high yield. The IR spectra of the soluble polymers showed the characteristic absorption of a carbonyl group of ketone 1706cm^{-1} , a carbon-carbon double bond at 1668 and 1649cm^{-1} , and a vinyl ether linkage at 1271cm^{-1} . Figure 2 shows the ^1H -NMR spectrum of the polymer (polymerization with 1 mol% of $\text{CH}_3\text{SO}_3\text{H}$, run 6 in Table 1) with the assignment for various signals. Two signals at $\delta 4.7$ - 5.0 and 5.6 - 5.8 ppm assignable to the different olefinic protons were observed. The signal corresponding to the methyl protons attached to a carbon-carbon double bond appeared at $\delta 1.71$ ppm. In the ^{13}C -NMR spectrum, the signal at $\delta 114.8$ ppm due to the acetal carbon of 4 completely disappeared, whereas the signal at $\delta 205.6$ ppm due to the carbonyl carbon was observed. These spectra indicated that 4 underwent quantitative ring-opening polymerization, and that the polymer consisted of both units 6 and 7 as shown in scheme 1.

In the polymerization for longer reaction

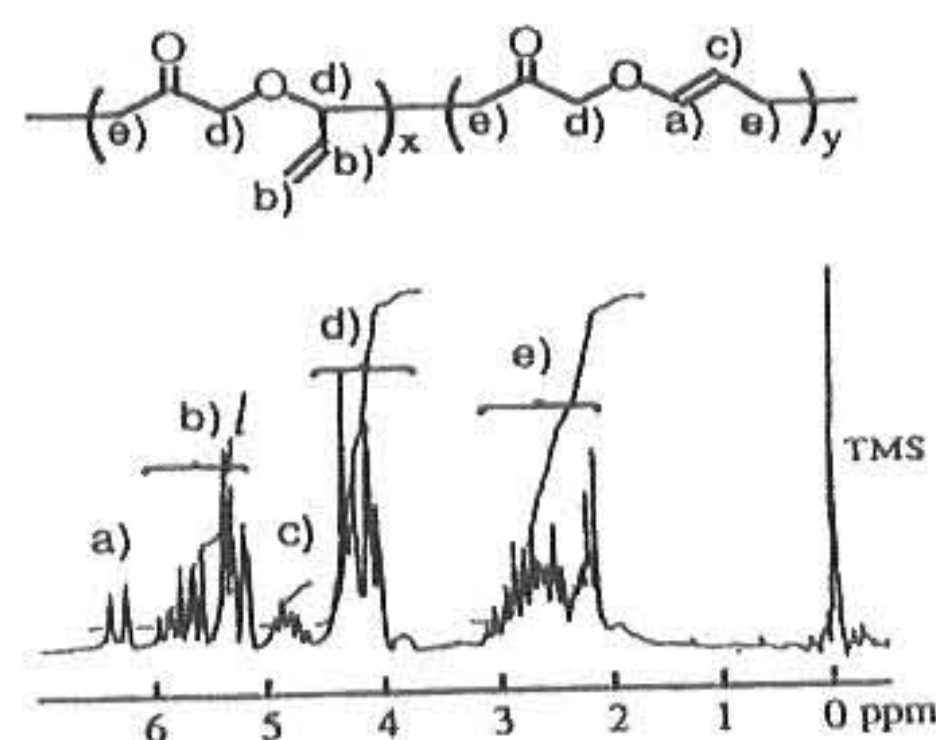
time (run 3 vs. 4, and run 6 vs. 7), unexpected signals at around $\delta 1.0$ ppm, which could be assigned as the aliphatic methyl and methylene group, appeared in the $^1\text{H-NMR}$. Simultaneously, the content of units **6** and **7** in the polymer were shown to decrease from 87 to 56% (run 3 vs. 4) and from 84 to 62% (run 6 vs. 7), respectively, by the $^1\text{H-NMR}$ analysis. Further cationic reaction of carbon-carbon double bond in the unit **6** and **7** would take place because of the low concentration of **4**. This is probably because further cationic reaction took place with the highly reactive carbon-carbon double bonds in the polymer. Accordingly, less reactive carbon-carbon double bonds in the polymer would be expected not to cause the undesired further cationic reaction of the polymer. Thus, an ethenyl group was introduced into the monomer instead of the isopropenyl group to reduce the side reaction. 2-Ethenyl-4-methylene-1,3-dioxolane(**5**) was prepared from acrolein and epichlorohydrin in the same two steps (scheme 2). The desired cyclic acetal **5** containing two carbon-carbon double bonds was obtained 52% yield.

Table 2. Cationic Polymerization of **5**^a

Run	Catalyst(Mol%)	Time (h)	Yield ^b %	M_n^c	mole ratio ^d x : y
1	BF_3OEt_2 (2)	0.5	76 ^e	--	--
2	BF_3OEt_2 (1)	3	64 ^e	--	--
3	$\text{CF}_3\text{SO}_3\text{H}$ (2)	1	62 ^e	--	70 : 30
4	$\text{CH}_3\text{SO}_3\text{H}$ (2)	1	20	1300	70 : 30
5	$\text{CH}_3\text{SO}_3\text{H}$ (2)	8	63	3000	70 : 30
6	$\text{CH}_3\text{SO}_3\text{H}$ (2)	16	78	4000	70 : 30
7	$\text{CH}_3\text{SO}_3\text{H}$ (1)	1	32	1200	74 : 26

^a Polymerization was carried out in dichloromethane at -78° ^b Insoluble in *n*-hexane^c By GPC calibrated with standard polystyrene^d Estimated by $^1\text{H-NMR}$ using benzene as an internal standard^e Crosslinked polymer.

Polymerization of **5 with some cationic initiators** : The polymerization of **5** was attempted with some cationic initiators, i.e.,

Figure 3. $^1\text{H-NMR}$ spectra of polymer (run 6, Table 2)

BF_3OEt_2 , $\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$. The results are summarized in Table 2. Only crosslinked polymers were obtained with BF_3OEt_2 and $\text{CF}_3\text{SO}_3\text{H}$ even at -78°C , whereas soluble polymers were obtained with $\text{CH}_3\text{SO}_3\text{H}$ in high yield. On the other hand, the polymerization of **5** did not proceed in the case of CF_3COOH as initiator.

The IR spectra of the soluble polymers showed the characteristic absorption of a carbonyl group of ketone at 1723cm^{-1} , a carbon-carbon double bond at 1684 and 1642cm^{-1} , and a vinyl ether linkage at 1276cm^{-1} . Figure 3 shows the $^1\text{H-NMR}$ spectrum of the obtained polymer (polymerization with 2 mol% of $\text{CH}_3\text{SO}_3\text{H}$, run 6 in Table 2) with the assignment for the various signals. Signals at $\delta 5.53$ – 5.17 and 6.23 ppm assignable to the different olefinic protons were observed. In the $^{13}\text{C-NMR}$ spectrum, the signal at $\delta 114.8$ ppm due to the acetal carbon of **5** completely disappeared, whereas the signal at $\delta 205.6$ ppm due to the carbonyl carbon was preserved. These spectra indicate that **5** undergoes quantitative ring-opening polymerization, and that the obtained polymer consists of the two units **6** and **7**. In the polymerization of **4**, unexpected signals around $\delta 1.0$ ppm in $^1\text{H-NMR}$ spectrum appeared with elapse of time, while the content of carbon-carbon double bonds in the polymer decreased. In the polymerization of **5**, however, the signal around $\delta 1.0$ ppm could not be observed, and the signal intensities from units **6** and **7** did not decrease with

time. This can be attributed to the less reactive ethenyl group in the polymer as compared to the isopropenyl group in the polymers obtained from 4. Thus, ethenyl group in the polymer probably does not undergo further cationic reactions.

4. Conclusions

On the basis of these results, polymerization is initiated by the addition of proton to the exo-methylene group of cyclic acetals 4, 5 to form carbocation intermediate, which undergoes ring-opening accompanying isomerization to keto group to afford more stable alkenyl-oxy cation. Propagation proceeds by electrophilic attack of each contributing structure to the 4-methylene group of monomers 4, 5 and continues in a chain reaction manner to form the polymer consisting of two units 6, 7. In the polymerization of 4 for longer reaction time, unexpected signals at around $\delta 1.0$ ppm in the $^1\text{H-NMR}$ show that the intramolecular back-biting reaction might proceed besides the intermolecular propagation reaction in the lower initial monomer concentration. In the polymerization of 5, however, the signal at around $\delta 1.0$ ppm in the $^1\text{H-NMR}$ could not be observed. This can be attribute to the less reactive ethenyl group in the polymer as compared to the isopropenyl group in the polymers obtained from 4.

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