# Selective Cationic Addition Polymerization of 2,4-Dimethylene-1,3-dioxolane by a Common Lewis Acid. Synthesis of Vinyl Ether–Pendant Polymer under Cationic Polymerization Conditions

**Tsutomu Yokozawa,[†] Ryoji Hayashi, and Takeshi Endo[*]**

*Research Laboratory of Resources Utilization,*
*Tokyo Institute of Technology, Nagatsuta, Midori-ku,*
*Yokohama 227, Japan*

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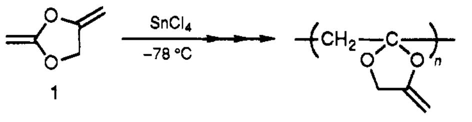
The development of polymerization of functional monomers containing specific reactive groups has led to the production of many kinds of functional polymers. Recently, it has become possible to carry out the cationic[1] or anionic[2] polymerization of monomers with two cationically or anionically polymerizable groups to provide new functional polymers when such polymerizable groups are different in structure (e.g., epoxy-functionalized styrene or vinyl ether). However, there are few documented examples of selective ionic polymerization of a monomer with two similar polymerizable groups except for the anionic polymerization of divinylbenzene.[3] This type of monomer could be prepared easily in contrast to the monomer with two different polymerizable groups, since the two similar polymerizable groups in the monomer could be prepared simultaneously. Herein, we report the selective cationic addition polymerization of 2,4-dimethylene-1,3-dioxolane (1),[4] which contains two carbon–carbon double bonds which are highly polymerizable by cations, one of a ketene acetal type and the other of a vinyl ether type. From 1 a new functional polymer having a vinyl ether structure in the side chain can be made.



The cationic polymerization of 1 was carried out by $SnCl_4$, $AlEtCl_2$, and $BF_3OEt_2$ in dichloromethane or toluene. The polymers obtained were purified by precipitation in hexane.[5] Table I summarizes the results. The product obtained with $SnCl_4$ in dichloromethane ($[1]_0$ = 1.0 M) at 25 °C for 12 h was only cross-linked polymer (entry 1) but that at −78 °C for 10 h consisted of soluble polymer and cross-linked polymer (entry 2). Further, the polymerization was carried out at low monomer concentration ($[1]_0$ = 0.33 M) for a short time (1 h) to obtain only soluble polymer in high yield (entry 3). $AlEtCl_2$ and $BF_3OEt_2$ gave also soluble polymers under this condition, although the yields of these polymers were lower than with $SnCl_4$ (entries 6 and 7 vs entry 3). The more polar dichloromethane gave better results concerning the polymer yield and molecular weight than the less polar toluene (entry 3 vs entry 4). Furthermore, the polymer molecular weight increased with decreasing amounts of catalyst (entry 3 vs entry 5).

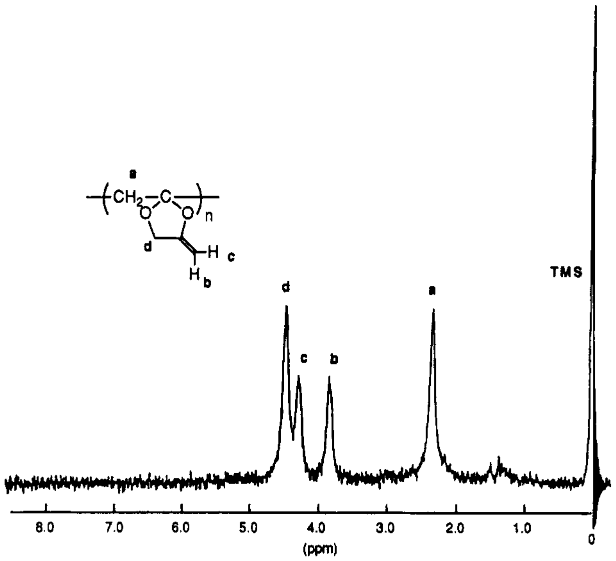


**Figure 1.** 60-MHz $^1H$ NMR spectrum of the polymer of 1 in $CDCl_3$.

In the IR spectra, two characteristic absorptions of a carbon–carbon double bond at 1690 and 1685 cm$^{-1}$ were observed in 1, whereas an absorption at 1685 cm$^{-1}$ was observed in the soluble polymers. There was no absorption attributable to a carbonyl group at 1740 cm$^{-1}$, which was observed in the spectrum of the polymer formed by radical ring-opening polymerization of 1.[4] Figure 1 shows the $^1H$ NMR spectrum of the polymer with the assignment for various signals. The signal of the 2-methylene protons of 1 at 3.39 ppm disappeared completely, and a new signal assignable to the methylene protons of the repeating polymerized C=C units appeared at 2.14–2.53 ppm in the polymer. On the other hand, the signals of 4-methylene protons at 4.00–4.20 and 4.45–4.62 ppm and of 1,3-dioxolane ring protons at 4.62–4.77 ppm of 1 were all slightly shifted upfield in the polymer. The $^{13}C$ NMR spectrum of the polymer showed the signals corresponding to C=C of the 4-methylene group at 77.6 and 156.0 ppm and the characteristic signal due to the acetal carbon at 111.4 ppm.[6] These spectral data indicate that 1 underwent selective addition polymerization of the 2-methylene group (C=C of the ketene acetal moiety) while retaining the 4-methylene group (C=C of the vinyl ether moiety).[7]

The polymerization of 2,5-dimethylene-1,3-dioxane (2)[4] was also carried out under the same conditions of the cationic polymerization of 1. However, only cross-linked polymer was obtained. This may show why 1 polymerizes selectively without cross-linking. It can therefore be presumed that the two nonconjugated double bonds of 2 polymerize simultaneously to afford cross-linked polymer,

**Table I**
**Cationic Polymerization of 1**

| entry | catalyst ($[cat.]_0$, mM) | solvent | $[1]_0$, M | temp, °C | time, h | yield,[a] % | $\bar{M}_n$[b] | $\bar{M}_w/\bar{M}_n$[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | $SnCl_4$ (20) | $CH_2Cl_2$ | 1.0 | 25 | 12 | 60[c] | | |
| 2 | $SnCl_4$ (20) | $CH_2Cl_2$ | 1.0 | −78 | 10 | 48 (26)[c] | | |
| 3 | $SnCl_4$ (6.6) | $CH_2Cl_2$ | 0.33 | −78 | 1 | 91 | 7400 | 1.68 |
| 4 | $SnCl_4$ (6.6) | $PhCH_3$ | 0.33 | −78 | 1 | 74 | 6100 | 1.71 |
| 5 | $SnCl_4$ (1.7) | $CH_2Cl_2$ | 0.33 | −78 | 1 | 63 | 11400 | 1.68 |
| 6 | $AlEtCl_2$ (6.6) | $CH_2Cl_2$ | 0.33 | −78 | 1 | 60 | 7500 | 1.55 |
| 7 | $BF_3OEt_2$ (6.6) | $CH_2Cl_2$ | 0.33 | −78 | 1 | 33[d] | 1000 | 2.79 |

[a] Insoluble in hexane. [b] By GPC calibrated with standard polystyrene. [c] Cross-linked polymer. [d] Soluble in hexane.

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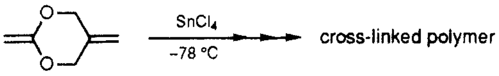
whereas one of the two double bonds conjugated through the oxygen atom in 1 acts as an electron-donating group and then decreases polymerizability to produce soluble polymer.



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In summary, the present work has demonstrated that a monomer with two similar polymerizable groups can be polymerized selectively with common Lewis acids. The obtained functional polymer containing polymerizable vinyl ether groups will be able to undergo cross-linking with Lewis acid for materialization or easy addition of other functional groups. Studies directed toward the function and availability of this polymer are currently under way.

## References and Notes

† Present address: Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan.

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(5) To the solution of 1 (0.196 g, 2 mmol) in dichlormethane (4 mL) was added the solution of $SnCl_4$ (4.7 μL, 0.04 mmol) in dichloromethane (2 mL) at −78 °C under an argon atmosphere. After 1 h, the polymerization was quenched with triethylamine, and the solution was poured into hexane (150 mL) to obtain the polymer as a white powder.

(6) The other signals were also observed at 44.9 (the methylene carbon of the backbone) and 66.6 (the methylene carbon of the 1,3-dioxolane ring) ppm.

(7) It has been reported that the cationic polymerizations of 2-methylene-1,3-dioxolane[8] and 4-methylene-1,3-dioxolane[9] proceed primarily by the carbon–carbon double bond addition, whereas the cationic polymerizations of 2,2-dimethyl- or 2-methyl-4-methylene-1,3-dioxolane[9] mainly take place by acetal ring opening to give a polyketoether.

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**Registry No.** 1 (homopolymer), 131491-72-0; 2 (homopolymer), 126659-42-5; $SnCl_4$, 7646-78-8; $AlEtCl_2$, 563-43-9; $BF_3OEt_2$, 109-63-7.