

Thianthrene 양이온 라디칼에 대한 비닐과 실릴 유도체의 반응성

禹熙權* · 宋善廷 · 梁秀妍 · 金煥基†

전남대학교 자연과학대학 화학과

† 삼양중앙연구소

(1996. 2. 3 접수)

Reactivity of Vinyl and Silyl Derivatives toward Thianthrene Cation Radical

Hee-Gweon Woo*, Sun-Jung Song, Soo-Yeon Yang, and Whan-Gi Kim†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

† Samyang Group R&D Center, Taejon 305-348, Korea

(Received February 3, 1996)

Conduction of oxidatively doped polymers like polythiophene and polypyrrole results when polarons (cation radicals) and bipolarons (dications) migrate along the conjugated polymer chain.^{1a} Little is known for the reactions of organic cation radicals with alkenes and alkynes despite of their important role in various organic reactions.^{1bc} A few examples of the addition of cation radicals such as $R_2NH^{+\cdot}$ and $t\text{-BuOH}^{+\cdot}$ to alkenes in the gas phase are known, and cation radicals are anticipated to be more electrophilic than neutral radicals.² There are some examples of the use of carbocation radical as an initiator for olefin polymerization.³ Nonetheless, polymerization of alkenes initiated by direct addition of a cation radical to the alkenes is not a common reaction. While carbocation radicals are generally *in situ*-generated or barely synthesized by anodic electrocrystallization, thianthrene cation radical perchlorate **1**, $[\text{Th}]^{+\cdot} \text{ClO}_4^-$ crystal,⁴ with moderate storage life can be easily prepared. The reactions of **1** have been so far limited to the addition and oxidation. The reactivity studies of **1** toward various nucleophiles including amines, aromatics, ketones, alkenes, alkynes, oximes, hydrazonitriles, organometallic complexes, etc. are found in the literature.⁵ Shine *et al.* described that **1** reacts with terminal or internal alkenes and alkynes to just form a 2 : 1 adduct

without isomerizing or polymerizing these unsaturated species.^{5f} However, we recently reported the polymerization of styrene and alkyl vinyl ether initiated by **1**.⁶ In the present paper we wish to report the reactivity study of various vinyl and silyl derivatives toward **1** in order to find new types of polymerization and/or reaction of them.

EXPERIMENTAL SECTION

Materials and instrumentation. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by the Elemental Analysis Center of the Korea Basic Science Institute, Seoul, Korea. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using chloroform-*d*/chloroform as a reference at 7.24 ppm downfield from TMS. Solid-state proton NMR spectra were obtained by the Solid state NMR Center of the Korea Basic Science Institute, Seoul, Korea. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC Liquid Chromatograph. The calibrant (monodisperse polystyrene)

and the sample were dissolved in THF and separately eluted from an Ultrastayragel GPC column series (sequence 10^3 , 10^4 , 10^5 , 10^6 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570. Methyl methacrylate and styrene (Aldrich Chemical Co.) were washed with aqueous 5% sodium hydroxide (to remove inhibitor), washed with distilled water, dried over magnesium sulfate, and distilled at reduced pressure before use. Acrylonitrile (Aldrich Chemical Co.) was washed with dilute sulfuric acid, washed with aqueous sodium carbonate, dried over magnesium sulfate, and distilled before use. Vinyltrimethoxysilane, 2-vinylpyridine, and 4-vinylpyridine (Aldrich Chemical Co.) were distilled at reduced pressure before use. Ethyl vinyl ether (Aldrich Chemical Co.) was distilled before use. Thianthrene cation radical perchlorate⁴, 2:1 adduct of thianthrene cation radical to phenylacetylene,^{5f} poly(phenylacetylene)⁷ ($M_n=15000$, $M_w=21000$, $M_w/M_n=1.4$), and poly(phenylsilane)⁸ ($M_n=1450$, $M_w=2160$, $M_w/M_n=1.5$), were prepared according to the literature procedure. (*Warning! Thianthrene cation radical perchlorate may be shock-sensitive and should be carefully handled with suitable protection.*)

Reaction of 1 with 2-vinylpyridine: preparation of 2:1 adduct (2). To a dark purple solution of 1 (1.14 g, 3.16 mmol) in methylene chloride (15 mL) was added 2-vinylpyridine (1.16 mL, 10.8 mmol) under a stream of nitrogen. The dark purple color faded with time, but did not completely disappear. After being stirred at room temperature for 24 h, volatiles were removed on a rotatory evaporator, and the residue was washed well with chloroform and dried at reduced pressure to yield 1.13 g (1.53 mmol, 85% based upon 1/2 of 1) of pale yellow solid 2 (mp 160–162 °C, dec) which was insoluble in most organic solvents. Anal. Calcd for $C_{31}H_{23}NO_3Cl_2S_4$: C, 50.54; H, 3.15. Found: C, 51.05; H, 3.84. IR (KBr pellet, cm^{-1}): 1070 s (ClO_4^-). Solid-state 1H NMR (δ , 300 MHz): 2.0–3.5 (br, $CHCH_2$), 6.5–8.0 (br, ArH).

Reaction of 1 with 4-vinylpyridine: preparation

of 2:1 adduct (3). 4-Vinylpyridine (1.16 mL, 10.8 mmol) was added to a dark purple solution of 1 (1.14 g, 3.61 mmol) in methylene chloride (15 mL) under a stream of nitrogen. The dark purple color was slowly discolored, but did not entirely vanish. After 24 h, removal of volatiles, washing with chloroform, and drying at reduced pressure afforded 1.17 g (1.59 mmol, 88% based upon 1/2 of 1) of pale yellow solid 3 (mp 198–200 °C, dec) which was insoluble in most organic solvents. Anal. Calcd for $C_{31}H_{23}NO_3Cl_2S_4$: C, 50.54; H, 3.15. Found: C, 51.66; H, 3.99. IR (KBr pellet, cm^{-1}): 1070 s (ClO_4^-). Solid-state 1H NMR (δ , 300 MHz): 2.0–3.5 (br, $CHCH_2$), 6.5–8.0 (br, ArH).

Reaction of styrene with 2. Styrene (2.06 mL, 18.0 mmol) was added to a suspension of 2 (0.66 g, 0.9 mmol) in methylene chloride (10 mL) at 0 °C under a stream of nitrogen. After being stirred for 48 h, no polymerization of styrene was observed. Similarly, the polymerization of styrene with 3 under the same reaction condition was not occurred, judged by 1H NMR spectroscopy.

Reaction of ethyl vinyl ether with 2:1 adduct of 1 and phenylacetylene. Ethyl vinyl ether (1.72 mL, 18.0 mmol) was charged to a suspension of 2:1 adduct of 1 and phenylacetylene (0.66 g, 0.9 mmol) in methylene chloride (10 mL) at 0 °C under a stream of nitrogen. After 48 h, ethyl vinyl ether was found not to be polymerized. Styrene was not polymerized by 2:1 adduct of 1 and phenylacetylene under the same reaction condition.

Polymerization of styrene with 1 in the presence of 4-vinylpyridine. Styrene (2.06 mL, 18.0 mmol) and 4-vinylpyridine (0.02 mL, 1.8 mmol) were added to a dark purple solution of 1 (56.8 mg, 0.18 mmol) in methylene chloride (2 mL) at 0 °C under a stream of nitrogen. The reaction turned light yellow, and the reaction medium became gradually viscous. After being stirred at room temperature for 24 h, the polymer was precipitated in methanol, filtered off, and dried to yield 0.13 g (7%) of off-white powder having $M_w=3900$ and $M_n=2500$. The 1H NMR and IR data were identical with the literature.⁶

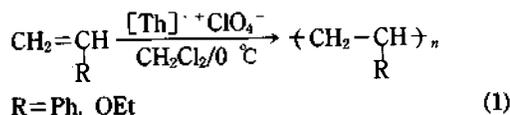
Reactions of olefins with 1. As a typical experi-

ment, 4-vinylpyridine (1.16 mL, 10.8 mmol) was added to a dark purple solution of **1** (69.5 mg, 0.22 mmol) in methylene chloride (5 mL) at 0 °C under a stream of nitrogen. The dark purple color did not fade with time and remained throughout the reaction. After being stirred for 24 h, no polymerization of 4-vinylpyridine resulted. Similarly, 2-vinylpyridine, acrylonitrile, methyl methacrylate, and vinyltrimethoxysilane were not polymerized by **1** under the same reaction condition, judged by ¹H NMR spectroscopy. The cation radical **1** neither added to acrylonitrile, methyl methacrylate, vinyltrimethoxysilane, and poly(phenylacetylene).

Reactions of silanes with 1. As a typical experiment, to a dark purple solution of **1** (1.14 mg, 3.61 mmol) in methylene chloride (15 mL) was added 1,2-diphenyldisilane (2.57 g, 12.0 mmol) under a stream of nitrogen. No color change was observed during the reaction. After being stirred for 48 h, it turned out that **1** did not form an adduct with disilane. Similarly, **1** did not add to phenylsilane, benzylsilane, and poly(phenylsilane) under the same reaction condition, judged by ¹H NMR spectroscopy. No appreciable change of molecular weights of poly(phenylsilane) before and after the reaction was observed.

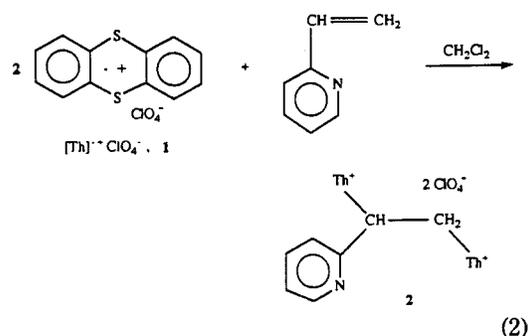
RESULTS AND DISCUSSION

Thianthrene cation radical perchlorate **1** is a highly reactive species yet having moderate storage life and can react with many reagents in a number of ways.⁵ **1** is reported to just add to alkenes and alkynes without polymerizing them.^{5f} However, we found earlier that **1** can initiate the polymerization of styrene and ethyl vinyl ether (Eq. 1).⁶



The polymerization yield of styrene was previously found to be drastically decreased by adding phenylacetylene, implying that the the adduct formation could occur prior to the initiation of polymerization.^{6a} Masuda *et al.* reported a competing polymerization

between phenylacetylene and styrene catalyzed by transition-metal halides. They found that triple bonds are more reactive than double bonds in coordination polymerization pathway, but double bonds are more reactive in cationic polymerization.^{6b} Similarly, the polymerization yield of styrene was pronouncedly decreased by increasing the concentration of 4-vinylpyridine. The addition of **1** to the vinyl group of 2-vinylpyridine was occurred at a slower rate than that of 4-vinylpyridine leading to the formation of 1,2-adducts **2** and **3**, judged by the rate of color change of reaction medium and product precipitation (Eq. 2).



In fact, polymerization of 2-vinylpyridine with cupric acetate is reported to be much slower than that of 4-vinylpyridine.⁹ The 1,2-adducts **2** and **3** were insoluble in most organic solvents and could have similar structure. However, the information on the stereochemistry of the 1,2-adducts could not be obtained from the solid-state proton NMR spectra because of broadly overlap nature of the NMR peaks. The two S-bound thianthrene moieties in the 1,2-adducts **2** and **3** presumed to be in the *anti*-position each other, because two bulky thianthrene moieties with same positive charge could repel each other. Two thianthrene cation radicals may respectively add to the pyridyl and vinyl moieties of vinylpyridines to produce 1,5-adducts. However, it is less likely to occur because the addition breaks the aromaticity of the pyridyl moiety. Thus, although there is some chance to form such an adduct, the metastable 1,5-adduct could then transform into the more stable 1,2-adducts **2** and **3** to recover the aromaticity.

The first electron transfer from **1** to vinylpyridines to produce thianthrene and vinylpyridine cation radical could be less likely to take place because acidic molecules are known to be able to initiate the polymerization of vinylpyridine and vinylpyridium salts can be self-polymerized in solution.¹⁰ The adducts **2** and **3** could not initiate the polymerization of styrene and ethyl vinyl ether. It is known that dimethylamino radicals can add to styrene forming a 2 : 1 adduct,¹¹ and styrene perchlorate derivatives can initiate the polymerization of styrene.¹² The 2 : 1 adduct of **1** and phenylacetylene could not initiate the polymerization of styrene and ethyl vinyl ether. In fact, the cation radical **1** is a highly reactive species and is known to react with a nucleophilic species (ZH) with hydrogen to generate a Brønsted acid, HClO₄.¹³ The adducts **2** and **3** seem to be too stable to initiate the polymerization of styrene, ethyl vinyl ether, and vinylpyridines. The addition of **1** to poly(phenylacetylene) was not occurred due presumably to the steric and conjugation effects of the polymer chain. The cation radical **1** neither initiated the polymerization nor added to methyl methacrylate and acrylonitrile due probably to the electron-deficient nature of the vinyl derivatives. The cation radical **1** neither initiated the polymerization nor added to vinyltrimethoxysilane, which presumed to be the steric effect of the trimethoxysilyl group and the delocalization of the cation radical into the silyl group. It was found that **1** did not add to phenylsilane, although **1** is known to add to the aromatic ring of aromatic compounds with electron-donating group.^{5c,5h} Polysilanes with unusual optical and electronic properties due to σ -conjugation along the silicon backbone have the reactive Si-Si and Si-H bonds.¹⁴ The polysilane is known to be able to either lose or gain electrons with chemical or electrical means, being converted to cation- or anion- radicals, respectively.^{14c} However, we found that **1** could not add to 1,2-diphenyldisilane and poly(phenylsilane), suggesting the silanes are apparently too stable to form an adduct with **1**.

Three mechanisms for the initiation step of the

polymerization of styrene and ethyl vinyl ether could be considered: (A) bond-formation, (B) HX-generation and (C) electron transfer. Some conclusive description on the initiation mechanism seem to be premature at this time in liaison with the present study on the polymerizability and additivity trend of the vinyl derivatives. Various factors should be considered including steric and electronic effects (e.g., oxidation potentials of the vinyl derivatives). More than a single mechanism may be operating simultaneously, giving rise to a very complex situation. The detailed study on the initiation mechanism of the polymerization is currently in progress and will be the subject of a future paper.

CONCLUSION

This work describes the polymerizability and additivity study of various olefin and silane derivatives in relation to the polymerization of styrene and ethyl vinyl ether, initiated by thianthrene cation radical **1**. The 1,2-adducts of **1** to vinylpyridines have been newly prepared. **1** did not add to vinyltrimethoxysilane, methyl methacrylate, acrylonitrile, poly(phenylacetylene), primary silanes, 1, 2-diphenyldisilane, and poly(phenylsilane). In addition, **1** was not capable of initiating the polymerization of vinylpyridines, vinyltrimethoxysilane, methyl methacrylate, and acrylonitrile. Comments on the initiation mechanism of the polymerization were finally made.

Acknowledgment. This research was supported by the Korea Science and Engineering Foundation (1996).

REFERENCES

- (a) Heeger, A. J.; Smith, P. *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Academic Publishers: Dordrecht, The Netherlands, 1991; pp 141-210 and references cited therein. (b) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 156. (c) Ebersson, L. *Adv. Phys. Org. Chem.* **1976**, *12*, 1.

2. (a) Magdzinski, L.; Chow, Y. L. *J. Am. Chem. Soc.* **1978**, *100*, 2444. (b) Shine, H. J.; Bandlish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915.
3. (a) Mengoli, G.; Vidotto, G. *Makromol. Chem.* **1971**, *150*, 277. (b) Funt, B. L.; Severs, W.; Glasel, A. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2763. (c) Glasel, A.; Murray, K.; Funt, B. L. *Makromol. Chem.* **1976**, *177*, 3345. (d) Oberrauch, E.; Salvatori, T.; Cesca, S. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 345.
4. Shine, H. J.; Pitte, L. *J. Am. Chem. Soc.* **1962**, *84*, 4798.
5. (a) Shine, H. J.; Silber, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 1026. (b) Bandlish, B. K.; Padilla, A. G.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 2590. (c) Kim, K.; Hull, V. J.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2534. (d) Lochynski, S.; Shine, H. J.; Soroka, M.; Venkatachalam, T. K. *J. Org. Chem.* **1990**, *55*, 2702. (e) Kim, K.; Shine, H. J. *Tetrahedron Lett.* **1974**, 4413. (f) Shine, H. J.; Bandlish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915. (g) Hoque, A. K. M. M.; Lee, W. K.; Shine, H. J.; Zhao, D.-C. *J. Org. Chem.* **1991**, *56*, 1332. (h) Silber, J. J.; Shine, H. J. *J. Org. Chem.* **1971**, *36*, 2923. (i) Kim, Y. H.; Lee, D. W.; Lee, W. K. *Bull. Korean Chem. Soc.* **1995**, *16*, 1225.
6. (a) Woo, H.-G.; Kim, S.-Y.; Hong, L.-Y.; Kang, H.-G.; Ham, H.-S.; Kim, W.-G. *J. Korean Chem. Soc.* **1995**, *39*, 680. (b) Masuda, T.; Higashimura, T. *Macromolecules* **1979**, *12*, 9.
7. Woo, H.-G.; Harrod, J. F. Unpublished results.
8. (a) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (b) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047.
9. Tazuke, S.; Okamura, S. *J. Polym. Sci. Part A-1* **1966**, *4*, 141.
10. (a) Kargina, O. V.; Kabanov, V. A.; Kargin, V. A. *J. Polym. Sci. Part C* **1968**, *22*, 339. (b) Mielke, I.; Ringsdorf, H. *Makromol. Chem.* **1972**, *153*, 307.
11. Michejda, C. J.; Campbell, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 929.
12. Matyjaszewski, K. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 433.
13. Crivello, J. V.; Lee, J. L.; Conlon, D. A. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 145.
14. (a) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. J. *Organomet. Chem.* **1986**, *300*, 327. (d) Ziegler, J. M.; Fearon, F. W. G. *Silicon-based Polymer Science*; American Chemical Society: Washington, DC, 1990.