

## Thianthrene 양이온 라디칼에 의한 비닐단량체의 양이온 중합

禹熙權\* · 金淑娟 · 洪麗泳 · 姜幸求 · 咸喜錫 · 金煥基†

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## Cationic Polymerization of Vinyl Monomers Initiated by Thianthrene Cation Radical

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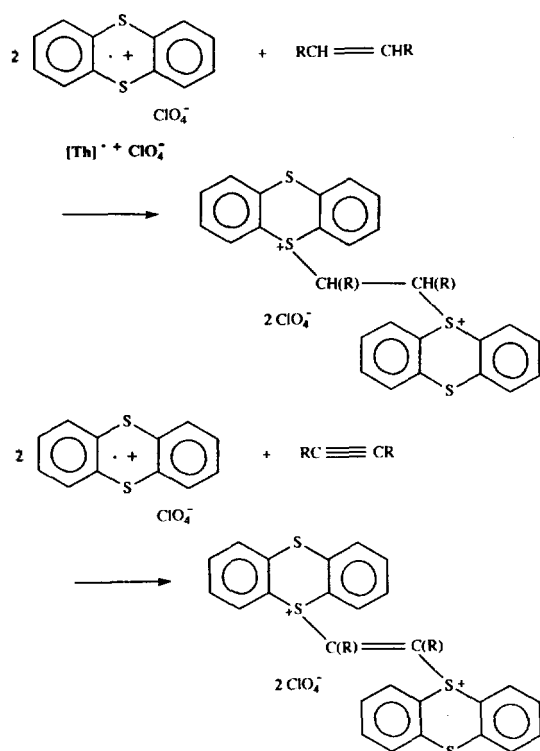
Cation radical chemistry has received ample attention because of its important role in various organic reactions.<sup>1</sup> Little is known for the reactions with alkenes and alkynes albeit organic cation radicals are reported to react with a variety of nucleophiles.<sup>1</sup> Some examples of the addition of cation radical such as  $R_2NH^+$  and  $t\text{-BuOH}^+$  to alkenes are known.<sup>2</sup> However, polymerization of alkenes initiated by addition of a cation radical is not a common reaction.<sup>1</sup>

The cationic polymerization of vinyl and heterocyclic monomers, which usually proceeds via ionic chain carriers, can be initiated by many agents including Lewis and Bronsted acids, oxonium salts and by ionizing radiation.<sup>3</sup> Mengoli<sup>4a</sup> was the first to report the persistent carbocation radical-initiated polymerization. There are some examples of the use of carbocation radicals in the initiation of polymerization.<sup>4</sup> By comparison, polymerization of vinyl monomers initiated by the cation radical of thianthrene, a heteroaromatic cycle containing two sulfur atoms in the para position, has not been reported. While carbocation radical crystals are synthesized by anodic electrocrystallization with difficulty or *in situ* generated,<sup>4</sup> thianthrene cation radical perchlorate crystals with moderate storage life can be easily prepared.<sup>5,6</sup> Thus, the reactivity

study of thianthrene cation radical toward various nucleophiles including amines, aromatics, ketones, alkenes, alkynes, organometallic complexes, oximes, *etc.* has been much done.<sup>5</sup> Thianthrene cation radical is reported to just form an adduct with alkenes and alkynes without polymerizing these unsaturated species (Scheme 1).<sup>5</sup> The thianthrene cation radical with two sulfur atoms may display different modes of reaction from the heteroatom-free carbocation radicals. In the present paper we report the polymerization of vinyl monomers initiated by thianthrene cation radical as a part of our research concerning the reactions of various agents with readily isolable, yet highly reactive species.

### 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. Infrared spectra were obtained using a Nicolet 520 P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using chloroform-*d*/chloroform as a refer-



nce at 7.24 ppm downfield from TMS. Number average molecular weights ( $M_n$ ) were determined by vapor pressure osmometry (VPO) in HPLC-grade chloroform using a Wescan Model 233100 osmometer and/or  $^1\text{H}$  NMR spectroscopy. 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. Phenylacetylene and 4-vinylpyridine (Aldrich Chemical Co.) were distilled at reduced pressure before use. Ethyl vinyl ether (Aldrich Chemical Co.) was distilled before use. Adduct of thianthrene cation radical to phenylacetylene<sup>5f</sup> and thianthrene cation radical perchlorate<sup>6</sup> were prepared according to the literature procedure. **Warning:**

Thianthrene cation radical perchlorate may be shock-sensitive and should be cautiously handled with appropriate protective measure.

**Polymerization of styrene with thianthrene cation radical perchlorate.** To a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) cooled to 0 °C was added styrene (2.06 mL, 18.0 mmol) under a stream of nitrogen. The reaction mixture turned brown within 5 min, and the reaction medium became then rapidly viscous with exothermicity. After stirring at room temperature for 24 h, the polymer was precipitated in methanol, filtered off, and dried to yield 1.58 g (87%) of off-white powder. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3050 m, 2900 s (vC-H), 1600 m, 1495 m, 1450 s, 1020 w, 730 s, 670 s.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.8~2.0 (br, 3H,  $\text{CHCH}_2$ ), 6.2~7.4 (br, 5H, ArH).  $M_n=2850$  (by VPO).

**Polymerization of styrene with thianthrene cation radical perchlorate in the dark.** Styrene (2.06 mL, 18.0 mmol) was added to a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) at 0 °C under a stream of nitrogen in the dark. The reaction mixture turned brown within 5 min, and the reaction medium became then rapidly viscous with exothermicity. After stirring at room temperature for 24 h, 1.54 g (85%) of off-white powder with  $M_n=2820$  (by VPO) was obtained by the same workup as described above. The  $^1\text{H}$  NMR and IR data were identical with those of the polystyrene obtained above.

**Acidity test for the solution of thianthrene cation radical perchlorate.** Thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) was dissolved in 5 mL of methylene chloride and left undisturbed. After 10 min, the violet solution was tested for residual acid with Litmus paper to display  $\text{PH}=5$ . The acidity of THF solution of thianthrene cation radical perchlorate was similarly found to be  $\text{PH}=5$ .

**Polymerization of styrene with thianthrene cation radical perchlorate in the presence of phenylacetylene.** Styrene (2.06 mL, 18.0 mmol) and phenyla-

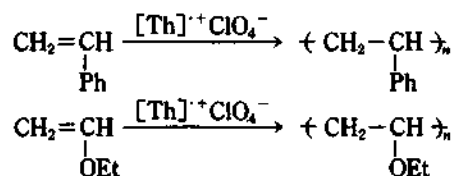
cetylene (0.02 mL, 0.18 mmol) were added to a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (2 mL) at 0 °C under a stream of nitrogen. The reaction mixture turned light yellow, and the reaction medium became gradually viscous. After stirring at room temperature for 24 h, 0.99 g (55%) of off-white powder with  $M_n=2690$  (by VPO) was obtained by the same workup as described above. The polymerization with phenylacetylene (0.2 mL, 1.8 mmol) yielded 0.03 g (1.6%) of off-white powder.

**Polymerization of ethyl vinyl ether with thianthrene cation radical perchlorate.** To a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) at 0 °C was added ethyl vinyl ether (1.72 mL, 18.0 mmol) under a stream of nitrogen. The reaction mixture immediately turned dark brown, and the reaction medium became very rapidly viscous with exothermicity. After stirring at room temperature for 24 h, the polymer was precipitated in methanol, filtered off, and dried to yield 1.10 g (85%) of light yellow powder. IR (KBr pellet,  $\text{cm}^{-1}$ ): 2950 s ( $\nu\text{C-H}$ ), 1375 m ( $\delta\text{C-H}$ ), 1100 s ( $\nu\text{C-O}$ ).  $^1\text{H NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 1.18 (br, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.61 (br, 2H, backbone  $\text{CH}_2$ ), 1.82 (br, 1H, backbone CH), 3.47 (br, 2H,  $\text{OCH}_2\text{CH}_3$ ).  $M_n=1880$ .

**Copolymerization of styrene and ethyl vinyl ether with thianthrene cation radical perchlorate.** To a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) at 0 °C was added ethyl vinyl ether (0.86 mL, 9.0 mmol) and styrene (1.03 mL, 9.0 mmol) under a stream of nitrogen. The reaction mixture immediately turned dark brown, and the reaction medium became very rapidly viscous with exothermicity. After stirring at room temperature for 24 h, the polymer was precipitated in methanol, filtered off, and dried to yield 1.31 g (85%) of pale yellow powder. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3050 s, 2960 s ( $\nu\text{C-H}$ ), 1807 m, 1716 m, 1600 m, 1445 m, 1450 s, 1375 m ( $\delta\text{C-H}$ ), 1100 s ( $\nu\text{C-O}$ ), 700 s, 500 s.  $^1\text{H NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.8~3.7 (br, all aliphatic CHn), 6.5~7.6 (br, ArH).  $M_n=2200$ .

## RESULTS AND DISCUSSION

Thianthrene cation radical perchlorate is a highly reactive species yet having moderate storage life and can react with many agents in a number of ways.<sup>5</sup> Thianthrene cation radical is reported to just add to alkenes and alkynes without polymerizing them (Scheme 1).<sup>9</sup> However, we found that the cation radical can polymerize styrene and ethyl vinyl ether as follows:



The molecular weights, determined by vapor pressure osmometry (VPO), were 2850 for polystyrene, 1880 for poly(ethyl vinyl ether), and 2200 for poly(styrene-co-ethyl vinyl ether). The polymerization proceeded even in the dark, implying the polymerization is not initiated by light. The polymerization yields drastically decreased with increase of molar ratio, [phenylacetylene] over [thianthrene cation radical perchlorate]: 87% for 0, 55% for 0.01, and 2% for 0.1 due probably to the adduct formation of thianthrene cation radical to phenylacetylene as shown in Scheme 1. The molecular weight data of the polymerization reactions were summarized in Table 1. The adduct of thianthrene cation radical to phenylacetylene could not

Table 1. Number average molecular weight data of polymerization of vinyl monomers initiated by thianthrene cation radical<sup>a</sup>

Monomer	Yield (%)	Mol wt <sup>d</sup>
Styrene	87	2850
Styrene <sup>c</sup>	85	2820
Styrene <sup>d</sup>	55	2690
Ethyl vinyl ether	85	1880
Styrene + Ethyl vinyl ether <sup>e</sup>	85	2200

<sup>a</sup>Monomer, 18 mmol; initiator, 0.18 mmol; methylene chloride, 5 mL for 24 h. <sup>b</sup>Measured with VPO in chloroform. <sup>c</sup>Performed in the dark. <sup>d</sup>Phenylacetylene (0.18 mmol) added. <sup>e</sup>1:1 molar ratio.



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