Preparation of Styrene Derivatives Containing Sulfide Group: Addition Reactions of Thiophenol and Its Derivatives to 1,4-Divinylbenzene

Eiichi KOBAYASHI,* Jian JIANG, Hiroyoshi MATSUMOTO,
and Junji FURUKAWA

*Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo, Noda, Chiba 278, Japan*

(Received April 13, 1990)

ABSTRACT: To prepare styrene derivatives containing a sulfide group such as 4-vinyl-1-[(2-phenylthio)ethyl]benzenes, the addition reactions of thiophenols to 1,4-divinylbenzene were carried out in the presence of AIBN or BPO. The maximum yields of the corresponding adducts were about 62% by the G.C. method. The competitive addition reaction of thiophenol to 1,4-divinylbenzene and the remaining vinyl group of the mono-adduct simultaneously took place to decrease the yield of the mono-adduct. The effects of the reaction time, reaction temperature and the additive in the course of the reaction are discussed based on gas chromatographic studies. The monomer reactivity ratio of the obtained mono-adduct was estimated by the radical copolymerization with MMA.

KEY WORDS Addition Reaction / Thiophenol / 1,4-Divinylbenzene / *p*-Arylthioalkylstyrene / 4-Vinyl-1-[(2-phenylthio)ethyl]benzene / 4-Vinyl-1-[(*p*-tolylthio)ethyl]benzene / 4-Vinyl-1-[(*m*-tolylthio)ethyl]benzene / Copolymerization / Monomer Reactivity Ratio /

Many kinds of styrene derivatives containing characteristic functional groups have been synthesized and used to prepare new advanced materials. For instance, Tsuruta *et al.*¹⁻³ studied the addition reactions of various amines to divinylbenzene by a lithium alkylamide catalyst to prepare styrene derivatives containing amine groups. The copolymerization with styrene was carried out to prepare copolymers with a sea-island microstructure or a lamellar microdomain which was found to be effective for antithrombogenic materials. Nakahama *et al.*⁴⁻⁵ reported also the preparation of styrene derivatives containing silyl groups. The silyl group was used to protect the reactive functional groups in the monomers toward anionic living polymerization of styrenes. Asahara *et al.*⁷ prepared al-

kythiomethylstyrene or arylthiomethylstyrene by a condensation reaction of chloromethylstyrene with sodium alkyl sulfide or sodium phenyl sulfide. The polymers composed of the sulfide monomers were highly reactive against an electron beam to develop a positive pattern.⁸

On the other hand, the addition reaction of a thiol group to an unsaturated carbon-carbon bond, which yields anti-Markownikoff type adducts in the presence of a radical initiator, is well known.⁹⁻¹¹ Screttas *et al.* carried out the addition reaction of thiophenol to olefin and diolefin to synthesize sulfide derivatives.¹² Another kinetic approach to the addition reaction of thiophenol to styrene showed^{13,14} that the reaction rate depends on the concentration of thiophenol. The rate determining step is the hydrogen transfer from

* To whom all correspondence should be addressed.

thiophenol to the intermediate carbon radical. However, few investigations have been conducted to prepare new styrene derivatives by the addition reaction.

The authors developed a new synthetic method for styrene derivatives containing a sulfide group by the addition reaction of thiophenol (TP) and its derivatives to 1,4-divinylbenzene (DVB) (Scheme 1).

Scheme 1.

In this paper, the authors deal with (i) synthesis of styrene derivatives containing a sulfide group, **2a**, **2b**, and **2c**, (ii) elucidation of the reaction mechanism, and (iii) the copolymerization of **2a** with methyl methacrylate and the estimation of *Q* and *e* values of the monomer **2a**.

RESULTS AND DISCUSSION

Addition Reactions of Thiophenol and Its Derivatives to DVB

Addition reaction mechanisms of thiophenols to styrenes are already examined in this laboratory.¹⁵ Here, addition reactions of thiophenols to DVB are extensively studied to obtain **2a**, **2b**, and **2c**. To synthesize new styrene derivatives containing a sulfide group, an addition reaction of **1a** with DVB was carried out at 75°C in benzene in the presence of small amount of initiators such as AIBN and BPO. An equimolar amount of **1a** and DVB with a small amount of the radical initiator was charged into a 50 ml round bottom flask

Figure 1. Relationship between reaction time and yield of **2a** in benzene at 75°C under nitrogen atmosphere. $[\text{DVB}]_0 = [\text{1a}]_0 = 0.34 \text{ mol l}^{-1}$; $[\text{Initiator}] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$. ●, AIBN; △, AIBN plus 1.87 ppm oxygen added against total monomer; □, BPO; ○, without initiator.

equipped with a three-way stopcock under nitrogen atmosphere. The reaction solution was colorless transparent from the beginning to the end of the reaction.

As shown in Figure 1, the yield of **2a** measured by G.C. method was significantly affected by the initiation mode. In the presence of the radical initiators, AIBN and BPO, the yield of **2a** rapidly increased up to about 65%, however, it remained about 20% without adding any initiator. A small amount of oxygen initiated the addition reaction, but a large amount of oxygen decreased the yield of **2a** as discussed later. The yield of **2a** reached a maximum of about 62% for 60 min, then decreased gradually with reaction time. After the reaction was stopped, **2a** was isolated with two methods, column chromatography or distillation under reduced pressure. For details, see EXPERIMENTAL. The isolated yield of **2a** was about 50%.

¹H NMR spectrum of the isolated **2a** is shown in Figure 2. There appeared three main peaks, characterized as absorptions of benzene rings (6.7–7.1 ppm, 9H), vinyl group (4.9–6.6 ppm, 3H) and methylene (2.6–3.2 ppm, 4H) of **2a**. In addition, no signals assignable to other structures than **2a** could be detected; e.g., no absorption peaks at 1.5 ppm and 3.5 ppm assigned for the methylene and methine of polymers of DVB and **2a**, respectively. In the

Figure 2. ^1H NMR spectra of **2a**, **2b** and **2c**, in CDCl_3 . TMS as standard.

^1H NMR spectra of **2b** and **2c**, besides the absorptions of benzene rings (6.7–7.1 ppm), vinyl group (4.9–6.6 ppm), and methylene (2.6–3.2 ppm), the characteristic methyl peaks appear at 2.2 ppm.

Figure 3 shows the IR spectrum of **2a**. The characteristic absorption peaks of the methylene group at 2940 and 2850 cm^{-1} , the strong absorption peaks of the vinyl group at 1630, 980, and 900 cm^{-1} , as well as the *p*-substituted and mono-substituted benzene rings appear at 820 and 730 cm^{-1} , respectively. With the comparison of the observed sulfur content of **2a**, 13.3% (Calcd 13.3%), it is clearly explained that the addition reaction of **1a** to DVB is capable of producing a novel styrene derivative containing the sulfide group, **2a**. In the IR spectra of **2b** and **2c**, besides the absorption peaks appeared in the IR spectrum of **2a**, methyl absorptions newly appear at 2995 and 1380 cm^{-1} .

The addition reaction of **1a** to DVB took place in the radical chain mechanism shown in Scheme 2, where I means a radical initiator.

Figure 3. IR spectra of **2a**, **2b**, and **2c**. Liquid film method.

Scheme 2.

With the repetition of reactions (3) and (4), the product **2a** was produced successively by the chain reaction. The reaction scheme is already discussed based on the kinetic method.¹⁶ However, the product **2a** possesses the reactive vinyl group toward thiophenol **1a** and active species for the polymerization. Accordingly, DVB simultaneously turns into products **2a** and **3a** as shown in Scheme 3. Indeed, the addition reaction of two moles of **1a** with one mole of DVB was reported to give the **3a** quantitatively.¹² Polymerization of DVB and **2a** would reduce also the yield of **2a**, if it occurred. However, only a small amount of polymers was recovered, since thiophenol can

act as an effective chain transfer reagent to prevent polymerizations.¹⁷ Consequently, the formation of the di-adduct **3a** may be the main factor to reduce the yield of the mono-adduct **2a**.

Scheme 3.

The thiophenol derivatives, *p*-toluenethiol and *m*-toluenethiol also reacted with DVB to give the corresponding novel adducts, **2b** and **2c** with about 50% of the isolated yield. These addition reactions behave quite the same as that of **1a** with DVB. ¹H NMR spectra of **2b** and **2c** are almost equal to that of **2a**, except the presence of the methyl group in the tolyl group at 2.2 ppm as already shown in Figure 2. The IR spectra showed characteristic absorption peaks of vinyl groups at 1630–1625 cm⁻¹, and the methyl and methylene groups at 2995, 2920, and 2850 cm⁻¹ (Figure 3). From these spectroscopic observations, as well as the sulfur content of **2b** and **2c**, it is realized that the structures of **2b** and **2c** are similar as those shown in Scheme 1.

Effect of Reaction Temperature

Figure 4 shows the effect of the reaction temperature on the addition reaction of **1a** with DVB under nitrogen atmosphere. The maximum yield of **2a** depends clearly on the reaction temperature, which is attained about 65% at 75°C for 50 min. However, the reaction time giving the maximum yields becomes longer with decrease of the reaction temperature. To obtain the maximum yield in a relatively short reaction time, it is necessary that the addition reaction of **1a** with DVB may be carried out at a high temperature, such as 75°C.

According to the temperature dependence of the initial reaction rate shown in Figure 4, the

Figure 4. Relationship between yield of **2a** and reaction temperature in benzene under nitrogen atmosphere. ●, 75°C; ○, 65°C; △, 55°C; [DVB]₀ = [1a]₀ = 0.34 mol l⁻¹; [AIBN] = 2.0 × 10⁻³ mol l⁻¹.

Figure 5. Effect of oxygen on the yield of **2a** in benzene under air atmosphere: ○, 75°C; □, 65°C; △, 55°C; ●, 75°C under nitrogen atmosphere. [DVB]₀ = [1a]₀ = 0.34 mol l⁻¹; [AIBN] = 2.0 × 10⁻³ mol l⁻¹.

apparent activation energy of the addition reaction of **1a** with DVB was estimated to be about 30 kcal mol⁻¹, which is almost the same as the activation energy of the decomposition of AIBN (about 31 kcal mol⁻¹).¹⁸ It seems that the reaction rate may be controlled by a decomposition rate of the radical initiator, so that the high reaction temperature would accelerate the addition reaction giving relatively high yield in a short reaction time.

Effect of Oxygen

It is generally believed that oxygen retards a radical chain reaction as a radical inhibitor. Figure 5 shows the relationship between the reaction time and the yield of **2a** in the addition reaction of **1a** with DVB under air at 55 to 75°C or under nitrogen atmosphere at 75°C.

In the presence of oxygen, a short induction period appears. The reaction rate under nitrogen is faster than that under air, since oxygen in air could disturb the chain reaction mentioned in Scheme 1. On the other hand, compared with the addition reaction under nitrogen atmosphere shown in Figure 4, at the relatively low temperature, *e.g.*, at 65°C and 55°C, the reaction rates obtained under air became higher than those under nitrogen atmosphere.

Actually, at a relatively low temperature oxygen oxidates mercaptan to form disulfide.¹⁹ In the presence of vinyl compounds, the intermediate thiyl radical attacks vinyl compounds giving adducts. Oxygen may accelerate the chain reaction involving thiols even at the low temperature.

Effect of Additive

Since vinyl groups of **2a** and DVB are able to participate in the homo- and copolymerization to reduce the yield of **2a**, a small amount of the additive as a polymerization inhibitor, *p*-*tert*-butylcatechol was added in the reaction mixture. Figure 6 shows the effects of the addition of *p*-*tert*-butylcatechol on the reaction.

When *p*-*tert*-butylcatechol was added in the amount of 100 to 2000 ppm, the reaction rate forming **2a** decreased, as well as the yield of **2a** also decreased below 60%, but no homo- and copolymers were detected. If *p*-*tert*-butylcatechol was not added to the reaction mixture, less than 5% of oligomers would be formed in benzene at 60°C.²⁰ In general, catechols stop markedly radical polymerizations of vinyl compounds. However, *p*-*tert*-butylcatechol does not affect so much the addition reaction of thiophenol to DVB, since the carbon radical probably reacts to both *p*-*tert*-butylcatechol and thiophenol. The reactivity of *p*-*tert*-butylcatechol is lower than that of thiophenol. The *p*-*tert*-butylcatechol radical is a stable one and may abstract hydrogen from thiophenol. Consequently,

Figure 6. Effect of the additive on the yield of **2a** in benzene at 75°C under nitrogen atmosphere. $[\text{DVB}]_0 = [\text{1a}]_0 = 0.34 \text{ mol l}^{-1}$; $[\text{AIBN}] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$. $[\text{Cat-echol}]$: ●, 0 ppm; ○, 100 ppm; □, 500 ppm; △, 2000 ppm.

Figure 7. Copolymerization of **2a** with MMA in benzene at 60°C under nitrogen atmosphere. $[\text{2a}]_0 + [\text{MMA}]_0 = 1.0 \text{ mol l}^{-1}$; $[\text{AIBN}] = 0.01 \text{ mol l}^{-1}$; yields were less than 10%. $[\eta]$ of copolymers in benzene at 30°C, 0.04–0.15 dl g⁻¹.

although the addition of *p*-*tert*-butylcatechol in the reaction mixture decreased the reaction rate before 90 min, the final yield of **2a** increased.

Copolymerization of **2a** with MMA

Since **2a** has a polymerizable vinyl group, the copolymerization of **2a** with methyl methacrylate was examined in benzene at 60°C in the presence of small amount of AIBN. The relationship between the monomer feed ratio and copolymer composition is shown in Figure 7, where the copolymer yields were restricted below 10% to elucidate the accurate monomer reactivity ratio.

In Figure 7, the line was drawn based on the monomer reactivity ratio taking $r_{2a} = 0.32$ and

$r_{\text{MMA}}=0.63$ calculated by means of Fineman–Ross method. From these monomer reactivity ratios, $Q_{2a}=0.69$ and $e_{2a}=-0.87$ were obtained based on the $Q-e$ rule. It is realized that **2a** has the polymerizability and the monomer reactivity ratio of **2a** to MMA is lower than that of *p*-methylstyrene to MMA, in which $r_{\text{P-Mst}}=0.44$ and $r_{\text{MMA}}=0.40$, $Q_{\text{P-Mst}}=1.10$, and $e_{\text{P-Mst}}=-0.63$.²¹ The intrinsic viscosities $[\eta]$ of these obtained copolymers were determined to be about 0.04 to 0.15 dl g⁻¹ in benzene at 30°C. The monomer **2a** has the sulfide group, so that the sulfide group may act as a chain transfer reagent like as the diphenyl sulfide, $C_{\text{tr}}=5.48 \times 10^{-3}$,²² and diethyl sulfide, $C_{\text{tr}}=2.7 \times 10^{-2}$.²³ **2a** is similar to the molecular structure of diphenyl sulfide and diethyl sulfide, since **2a** has the phenylthiomethylene group and consequently, the chain transfer constant of **2a** may be almost the same as that of diphenyl sulfide and diethyl sulfide, which is much higher than that of benzene, 1.8×10^{-6} .²³ Thus, **2a** reduces the molecular weight of the copolymers.

EXPERIMENTAL

Materials

Thiophenol (Wako Pure Chem. Co.), *p*-toluenethiol (Aldrich Chem. Co.), and *m*-toluenethiol (Wako Pure Chem. Co.) were purified by distillation under reduced pressure under nitrogen atmosphere. 1,4-Divinylbenzene (Hokkou Chem. Co.) and methyl methacrylate (Wako Pure Chem. Co.) were also purified by distillation under reduced pressure under nitrogen atmosphere before use. AIBN was purified by recrystallization in hexane. Solvent benzene was used by distillation after being degassed with bubbling nitrogen for 2 h.

Preparation of **2a**

In a four necked 200 ml round bottom flask equipped with a three-way stopcock, equimolar amount of benzene solutions of thiophenol and DVB, a small amount of a benzene solution of

AIBN were charged by hypodermic syringe under nitrogen atmosphere. The initial concentrations of thiophenol, DVB and AIBN are 1.25 mol l⁻¹, 1.25 mol l⁻¹, and 0.013 mol l⁻¹, respectively. The addition reaction was carried out at 65°C for 90 min under nitrogen atmosphere.

The adduct **2a** was isolated from the reaction mixture by two methods, column chromatography and distillation under reduced pressure. By column chromatography, the reaction mixture was evaporated to remove the solvent, then developed in the column filled with Silica gel (Wako Gel, Q-23, 100–200 mesh) and carbon tetrachloride as an eluent, and then purified by distillation under reduced pressure. The distillation method was performed under reduced pressure adding small amounts of polymerization inhibitors, thiophenol or anhydrous ferric chloride after removed the benzene solvent. The two methods have almost the same efficiency for isolating **2a**. The isolated yield of **2a**, 4-vinyl-1-[(2-phenylthio)ethyl]benzene, was about 50%; bp, 129–131°C/0.04 mmHg; $n_D^{25}=1.6211$; $m/z=240$; elementary analysis, Calcd: C, 80.0%; H, 6.7%; S, 13.3%. Found: C, 80.1%; H, 6.6%; S, 13.3%.

Preparation of **2b**

4-Vinyl-1-[(*p*-tolylthio)ethyl]benzene, **2b** was prepared in the same manner as above at 75°C for 115 min. Yield, about 50%; bp, 138°C/0.06 mmHg; $n_D^{25}=1.6110$; Elementary analysis, Calcd: C, 80.3%; H, 7.1%; S, 12.6%. Found: C, 80.0%; H, 7.2%; S, 12.5%.

Preparation of **2c**

4-Vinyl-1-[(*m*-tolylthio)ethyl]benzene, **2c**, was also synthesized in the same method described above at 75°C for 120 min. Yield, about 50%; bp, 126–127°C/<10⁻³ mmHg; $n_D^{25}=1.6115$; Sulfur content, Calcd, 12.6%; Found, 12.6%.

Copolymerization of **2a** with MMA

The copolymerization of **2a** with MMA was

carried out at 60°C in a sealed glass tube, where definite amounts of **2a**, MMA and AIBN with benzene were charged under nitrogen atmosphere. After polymerization, the reaction mixture was poured into a large amount of methanol to precipitate copolymers. The copolymers were washed with methanol several times and dried *in vacuo* overnight. The copolymer compositions were estimated from sulfur content of the copolymers by Schoeniger's method.²⁴

Measurements

The reaction course was monitored by gas chromatography using a silicon GE SE-30, 2m column and a flame ion detector. Column temperature, 250°C; injection temperature, 300°C; carrier gas flow, N₂, 32 ml min⁻¹. The retention time was recorded in a minute: thiophenol, 0.3; DVB, 0.4; **2a**, 6.3. Diphenyl sulfide was used as the external standard for the quantitative analysis of **2a** was not observed by gas chromatography under this condition. By changing the G.C. conditions, column temperature, 260°C; injection temperature, 330°C; carrier gas flow, N₂, 50 ml min⁻¹, **3a** was detected in the retention time, 56.3 min.

IR spectra were recorded with a Hitachi 260-50 infrared spectrometer and ¹H NMR was determined using a JEOL PMX-60si with the chemical shifts δ from TMS as 0 ppm. Mass spectra were recorded with a JMS D-300. The refractive index was measured by an Atago Abbe Refractometer 301 at 25°C. Sulfur content of these adducts **2a**, **2b**, and **2c** and the copolymers was determined by Schoeniger's method.²⁴

REFERENCES

1. Xue-fen Li, M. Maeda, and T. Tsuruta, *Makromol. Chem.*, **182**, 2445 (1981).
2. T. Narita, Y. Nitatori, T. Irie, and T. Tsuruta, *Makromol. Chem.*, **177**, 3255 (1979).
3. M. Maeda, Y. Nitatori, and T. Tsuruta, *Makromol. Chem.*, **181**, 2245 (1980).
4. T. Hatayama, K. Yamaguchi, A. Hirao, and S. Nakahama, *Polym. Prepr. Jpn.*, **34**, 190 (1985).
5. A. Hirao, K. Yamaguchi, K. Takenaka, K. Suzuki, S. Nakahama, and N. Yamazaki, *Makromol. Chem., Rapid Commun.*, **3**, 941 (1982).
6. A. Hirao, K. Takenaka, K. Yamaguchi, S. Nakahama, and N. Yamazaki, *Polym. Commun.*, **24**, 339 (1983).
7. T. Asahara, M. Seno, H. Kise, and H. Serita, *Seisan Kenkyu*, **24**, 253 (1973).
8. Toray Co., Jpn. Patent, S-59-90846.
9. F. W. Stacey and J. F. Harris, Jr., *J. Am. Chem. Soc.*, **85**, 963 (1963).
10. A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Am. Chem. Soc.*, **86**, 2877 (1964).
11. K. Griesbaum, A. A. Oswald, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **85**, 1969 (1963).
12. C. G. Screttas and M.-M. Screttas, *J. Org. Chem.*, **43**, 1064 (1978).
13. R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).
14. M. Onyszchuk and C. Sivertz, *Can. J. Chem.*, **33**, 1034 (1955).
15. E. Kobayashi, T. Obata, S. Aoshima, and J. Furukawa, *Polym. J.*, **22**, 803 (1990).
16. J. Jiang, E. Kobayashi, T. Obata, and J. Furukawa, *Polym. J.*, **22**, 963 (1990).
17. S. C. Barton, R. A. Bird, and K. E. Russell, *Can. J. Chem.*, **41**, 2737 (1963).
18. J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).
19. S. Oae, "Organic Sulfur Chemistry, Reaction Mechanism Section," Kagaku Doujin, Tokyo, 1982, p 264.
20. T. Obata, M. Sc. Thesis, Science University of Tokyo, Noda (1990).
21. J. Brandrup and E. H. Immergut, "Polymer Handbook," 3rd ed, John Wiley and Sons, New York, 1989, pp II-200, II-269.
22. K. Tsuda, S. Kobayashi, and T. Otsu, *Bull. Chem. Soc., Jpn.*, **38**, 1517 (1965).
23. J. Brandrup and E. H. Immergut, "Polymer Handbook," 2nd ed, John Wiley and Sons, New York, 1975, p II-59.
24. W. Schoeniger, *Mikrochim. Acta*, 123 (1955).