

## [Regular Paper]

## Retardation Effect of Sulfonic Acid on Thermal Radical Polymerization of Styrene

Jun-ichi NAKAJIMA<sup>†1)\*, †2)</sup>, Seiji TANIZAKI<sup>†1)</sup>, and Hideo TOMIOKA<sup>†2)</sup><sup>†1)</sup> Yokkaichi Laboratory, Hakuto Co., Ltd., 6-6-9 Betsumei, Yokkaichi, Mie 510-0007, JAPAN<sup>†2)</sup> Chemistry Dept. for Materials, Faculty of Engineering, Mie University,  
1515 Kamihama-cho, Tsu, Mie 514-8507, JAPAN

(Received March 31, 2002)

A new polymerization retarder was investigated as an alternative to highly toxic dinitrophenols for the styrene distillation process. Dodecylbenzenesulfonic acid (DBS) was found to reduce the initial rate of thermal radical polymerization of styrene. The molecular weight of polystyrene resulting from thermal polymerization was slightly higher in the presence of DBS than in the absence of DBS. 1-Phenyltetraline (**1**), obviously produced by isomerization of the initial Diels–Alder adduct of styrene (**4**), was also detected in the presence of DBS. These observations suggest that DBS behaves as an acid catalyst for the isomerization of **4** to **1**. The retardation effect can be explained as the reduction of the concentration of initiate radicals generated from molecular assisted homolysis of **4** and monomeric styrene. Although only sulfonic acid cannot completely replace highly toxic and reactive dinitrophenols, it can reduce the amount of dinitrophenols required.

**Keywords**Dodecylbenzenesulfonic acid, Polymerization retarder, Polymerization inhibitor,  
Thermal radical polymerization, Styrene**1. Introduction**

Molecules which suppress or inhibit the polymerization of monomers are classified either as inhibitors or retarders<sup>1)</sup>. Styrene, one of the most important monomers, undergoes spontaneous polymerization when heated even in the absence of initiators, and so various inhibitors or retarders have been developed<sup>2)</sup> to prevent undesired polymerization. In general, dinitrophenols such as 2,4-dinitrophenol (DNP) and 2,4-dinitro-6-*s*-butylphenol (DNBP) have been used commercially as in-process retarders for the styrene purification distillation process<sup>3)</sup>. Such dinitrophenols are effective polymerization retarders for styrene, but most of them are extremely toxic and highly reactive, so require special precautions for use. Therefore, a new retarder which is less toxic and reactive is highly desirable.

Several mechanisms by which aromatic nitro compounds retard thermal radical polymerization of styrene have been proposed, including migration of the  $\beta$ -hydrogen of the propagation radical to the nitro group of the retarder to form an oligomer with a terminal double bond<sup>4)</sup>, and addition of the propagation radical to the nitro group<sup>5),6)</sup> or aromatic ring<sup>7)</sup> of the nitro com-

pounds. However, the retardation mechanism of dinitrophenols is little understood. Our previous investigation of the retardation mechanism of dinitrophenols found that the phenolic OH group is important and the effect depends on the structure of the dinitrophenol<sup>8)</sup>. For example, the retardation effect of 2,6-dinitrophenol was slightly greater than that of 2,4-dinitrophenol, indicating that the acid dissociation constant ( $K_a$ ) of dinitrophenols may be related to the retardation mechanism. We also found that aryl- and alkylsulfonic acids exhibit similar retardation effects.

Here, we report our investigation of the retardation of styrene polymerization by aryl- and alkylsulfonic acids.

**2. Experimental Procedure****2.1. General**

<sup>1</sup>H-NMR spectra were recorded on a JEOL JNM-AL 300FT/NMR (nuclear magnetic resonance) spectrometer in CDCl<sub>3</sub> with Me<sub>4</sub>Si as the internal standard. Gel permeation chromatography was carried out on a Hitachi GPC (gel permeation chromatography) system equipped with a RI detector and Shodex GPC KF-804 (4.6 × 25 cm) column using polystyrene standards as the reference and tetrahydrofuran (THF) as the carrier solvent. Gas chromatography and mass spectra were

\* To whom correspondence should be addressed.

\* E-mail: nakajima-j@hakuto.co.jp

obtained on a HP-6890 GC (gas chromatography) system using a HP-1 cross-linked methyl siloxane capillary column (0.32 mm  $\times$  15 m, film thickness 0.25 mm) and flame ionization detector or mass selective detector.

## 2. 2. Material

2,6-Dinitro-6-*s*-butylphenol was purchased from SNPE (France). All other reagents were purchased from Tokyo Kasei Kogyo Co., Ltd. Styrene stabilized with *t*-butylcatechol was distilled under reduced pressure prior to each experiment.

## 2. 3. Measurement of Retarding Effect on Thermal Polymerization of Styrene

The effect of the retarders was evaluated by comparing polystyrene formation in the presence and absence of retarders. In a typical run, a 250 ml laboratory bottle (SHOT Glass DURAN labglas) equipped with N<sub>2</sub> gas inlet, vent and sample outlet valve (Omnifit Ltd.) was charged with 100 g of styrene and retarders. The mixture was degassed by purging with N<sub>2</sub> for 10 min. The bottle was then immersed into an oil-bath thermostatically controlled at 120  $\pm$  0.1  $^{\circ}$ C and heated with purging N<sub>2</sub> (80 ml/min). After 10 min, the temperature of the mixture reached at 120  $^{\circ}$ C; this time was considered time zero. An aliquot (about 2 g) of the mixture was removed from the bottle and weighed precisely. Methanol (20 ml) was added immediately to precipitate the polymer formed during this period. The precipitated polystyrene was filtered with a 1  $\mu$ m polytetra fluoroethylene (PTFE) membrane filter that was pre-weighed prior to use. The polymer was dried and weighed. Conversion was calculated from the weights of the sample and the polymer. The dried polymer was dissolved in THF and the molecular weight was determined by GPC.

The rate of polymerization was calculated from the slope of polymer conversion as a function of reaction time in the absence and presence of dodecylbenzenesulfonic acid (DBS). Polymer conversion in the presence of dinitrophenols was not linear, so the rate of polymerization was difficult to estimate during the 120 min. Therefore, the "instantaneous" rate of polymerization ( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ) at 60 min was calculated by dividing the polymer conversion at 60 min by 3600 s, and compared to evaluate the performance of various retarder compounds.

## 2. 4. Determination of Styrene Dimers

The filtrate separated by filtration was concentrated under reduced pressure and residual styrene dimers (**1-3**) were isolated by TLC (Merck plate coated with silica gel GF<sub>254</sub> 0.25 mm thick, hexane). Dimers **2** and **3** were not isolated in sufficient quantities to allow <sup>1</sup>H-NMR analysis and so were characterized only by GC-Mass. The concentrations of dimers were measured by GC (hydrogen-flame ionization detector: FID). About 1 g of mixture removed from the bottle was

cooled rapidly to 0  $^{\circ}$ C to halt polymerization and a THF solution of pyrene was added to the mixture as the internal standard.

1-Phenyltetralin (**1**), <sup>1</sup>H-NMR(CDCl<sub>3</sub>)  $\delta$  1.70-1.83 (m, 1H), 1.84-1.93 (m, 2H), 2.14-2.17 (m, 1H), 2.84-2.92 (m, 2H), 4.12 (dd, 1H, *J* = 6.06, 7.17 Hz, 1H), 6.82 (d, *J* = 4.41 Hz, 1H), 6.82-7.30 (m, 9H). MS *m/e* (relative intensity) 209 (M+1, 17.1), 208 (M+, 100), 180 (90.8), 179 (80.3), 178 (47.4), 165 (44.7), 152 (10.5), 131 (21.1), 130 (76.3), 104 (20.4), 91 (34.2), 89 (21.1).

1,2-Diphenylcyclobutane (**2**), MS *m/e* (relative intensity) 208 (M+, 2.3), 178 (3.7), 104 (100), 78 (10.9).

1-Methyl-3-phenylindane (**3**), MS *m/e* (relative intensity) 209 (M+1, 13.2), 208 (M+, 79.6), 193 (73.0), 178 (34.2), 165 (13.8), 130 (23.7), 115 (100), 91 (36.8).

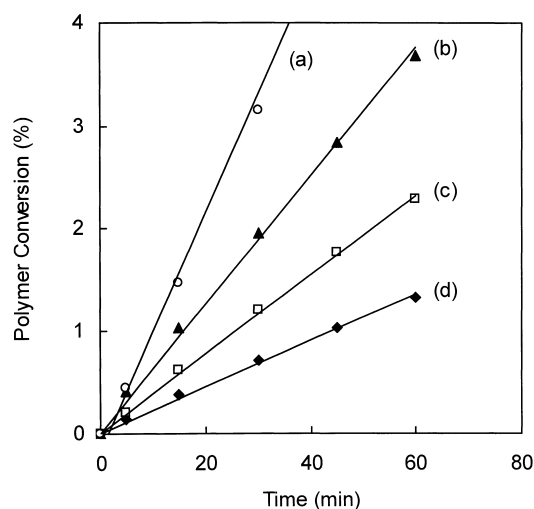
## 2. 5. Determination of DNBP Concentration

Accurately weighed mixture removed from the bottle was dissolved in xylene (10 ml) and residual DNBP was extracted with 10 ml of aqueous NaOH (0.5%). The concentration of DNBP in the aqueous phase was determined by UV/VIS spectroscopy (JASCO UBEST-500 spectrometer).

## 3. Results and Discussion

### 3. 1. Retardation Effect of DBS

The rate of polymerization of styrene at 120  $^{\circ}$ C was conveniently estimated from the slope of the yield of polymer as a function of reaction time at the initial stage of the polymerization when the linearity of the plot was fairly good (Fig. 1). The rate of polymerization decreased when dodecylbenzenesulfonic acid (DBS) was added to the mixture. In the presence of 100 ppm of DBS, the rate of polymerization was



(a) 0, (b) 100 ppm, (c) 200 ppm, (d) 1000 ppm.

Fig. 1 Effect of Dodecylbenzenesulfonic Acid on the Thermal Polymerization of Styrene at 120  $^{\circ}$ C

Table 1 Rate of Polymerization in the Presence and Absence of DBS

Reagent	Temp. [°C]	Concentration [ppm]	Rate of polymerization [ $\text{mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ]
DBS	120	100	10.2
		200	6.45
		1000	3.78
None	110	—	7.82
	120	—	19.3
	130	—	32.7
	140	—	54.9

Table 2 Rate of Polymerization in the Presence of Sulfonic Compounds at 120°C

Reagent	Concentration [ppm]	Rate of polymerization [ $\text{mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ]
DBS	100	10.2
<i>p</i> -toluene sulfonic acid	100	10.1
methanesulfonic acid	100	9.77
None	—	19.3
DB	100	16.1
DBS-Na salt	100	15.8
<i>p</i> -toluene sulfonic acid ethyl ester	100	17.1

reduced to half of the rate in the absence of DBS. The reduction of the rate depended on the concentration of DBS.

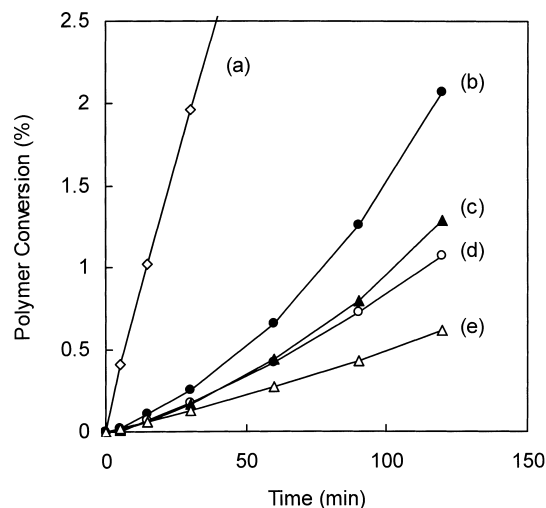
DBS reduced the rate of polymerization without any induction period, as if the polymerization temperature had been decreased (Fig. 1). As shown in Table 1, the rate of polymerization at 120°C in the presence of 100 ppm of DBS was essentially equal the rate of polymerization in the absence of retarder at 110–120°C. This result is in a marked contrast to that observed for polymerization in the presence of free-radical inhibitors where an induction period is usually observed<sup>9,10</sup>.

To investigate the origin of the retardation effect, the effect of the structure of the sulfonic derivatives was investigated (Table 2). *p*-Toluene sulfonic acid had a similar retarding effect to DBS, indicating that the length of alkyl chain is not important. Methane sulfonic acid also showed a similar effect.

In contrast, sodium salt of DBS (DBS-Na) and *p*-toluene sulfonic acid ethyl ester exhibited little retardation effect. Dodecyl benzene (DB) also exhibited no retardation effect. These observations clearly indicate that the free sulfonic acid group is required for retardation of styrene polymerization.

### 3.2. Comparison of Retardation Effects of DBS and Dinitrophenols

To evaluate the retardation effect of DBS, the effect was compared with that of dinitrophenols, which are typical styrene polymerization retarders. Figure 2 suggests that the retardation effect of DBS is signifi-



(a) DBS 100 ppm, (b) DNBP 100 ppm, (c) DNP 100 ppm, (d) DBS 50 ppm + DNBP 50 ppm, (e) DBS 50 ppm + DNP 50 ppm.

Fig. 2 Comparison of the Retardation Effects of DBS and Dinitrophenols

cantly smaller than those of dinitrophenols. For example, the rate of polymerization of DBS at 60 min was  $19.3 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ , whereas the rates for DNP and DNBP were  $1.63$  and  $1.84 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ , respectively.

However, a mixture of DBS and dinitrophenols had a much larger retardation effect than that expected from the individual components. Thus, the retardation effect of DNBP (Fig. 2(b)) was larger than that of only DBS (Fig. 2(a)). However, the addition of both DBS (50 ppm) and DNBP (50 ppm) showed a larger reduction in the polymerization rate than that of DNBP at the same concentration (Fig. 2(d)). A similar synergistic effect was observed for the combination of DBS and DNP (Fig. 2(e)).

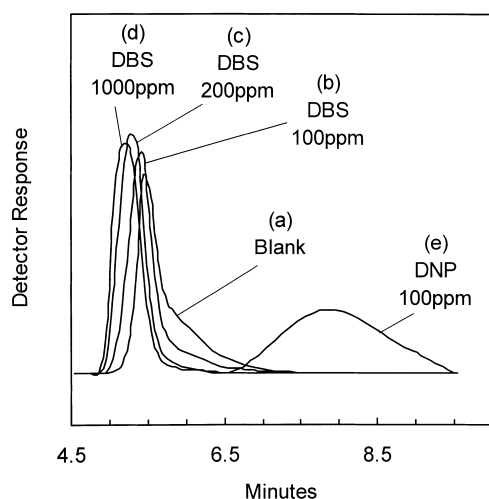
### 3.3. Effect of Retarder on the Molecular Weight of Polystyrene

Dinitrophenols may retard the polymerization of styrene by acting as chain-transfer agents<sup>1)</sup>, which quench styrene radicals leading to less reactive radicals. In the presence of these retarders, the polymer molecular weight is reduced because the propagation radical is quenched by the retarders before attacking another monomer to form a higher molecular weight polymer. If DBS acts as a chain-transfer agent in a similar manner, the molecular weight of the polymer is also expected to be reduced. To check this possibility, the molecular weight of polystyrene formed in the presence of DBS was determined by GPC and compared with that obtained in the absence and presence of DNP.

GPC showed a significant increase in elution time and polydispersity for polymer obtained in the presence of DNP (Fig. 3(e)) compared to unretarded polymer (Fig. 3(a)). This data clearly suggests that DNP is

acting as strong chain-transfer agent.

However, GPC of the polymer obtained in the presence of DBS showed no increase in elution time or polydispersity. It is rather surprising to note that the elution times decreased with increasing concentration of DBS. **Table 3** shows the number-average molecular weights ( $M_n$ ) and weight-average molecular weights ( $M_w$ ) calculated from the GPC trace. The  $M_n$  for polystyrene in the presence of 100 ppm of DBS at



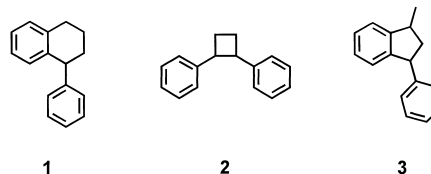
(a) Control, (b) DBS 100 ppm, (c) DBS 200 ppm, (d) DBS 1000 ppm, (e) DNP 100 ppm.

Fig. 3 Comparison of GPC Traces for Polystyrene Formed in the Presence of DBS and DNP at 120°C

30 min was 1.3 times higher than that of unretarded polystyrene, whereas the  $M_n$  in the presence of DNP decreased to 1/30. These results suggest that DBS does not act as chain-transfer agent to achieve retardation.

### 3.4. Product Analysis

To obtain more insight into the mechanism of DBS retardation, the filtrate separated from the mixture in methanol was analyzed by GPC. The filtrate should contain oligomer or products formed as a result of the reaction of initiate radical and retarder, which may provide important information on the retardation mechanism. The filtrate was distilled under reduced pressure to remove the remaining styrene monomer and methanol and the residue was dissolved in THF and analyzed by GPC. The GPC analysis exhibited a single peak at 11.35 min, which was estimated to have a molecular weight of around 200 by comparison with the reference polystyrene retention time. The main product separated by thin-layer chromatography (TLC) was determined to be 1-phenyltetralin (**1**). 1,2-Diphenylcyclobutane (**2**) and 1-methyl-3-phenylindane (**3**) were also confirmed as minor components by GC-MS (mass spectroscopy).



### 3.5. Relationship between Styrene Dimers and the Retardation Effect

The effect of the retarders on the concentration of

Table 3 Comparison of Molecular Weights of Polystyrene

Retarder	Concentration [ppm]	Time [min]	Molecular weight ( $\times 10^5$ )		
			$M_n$	$M_w$	$M_w/M_n$
DBS	100	15	7.68	9.89	1.29
		30	5.56	7.93	1.43
		45	5.32	8.10	1.52
		60	5.15	7.52	1.46
	200	15	11.3	12.9	1.14
		30	10.7	12.2	1.14
		45	9.88	11.4	1.15
		60	9.74	11.3	1.16
	1000	15	12.7	14.6	1.15
		30	12.1	13.7	1.13
		45	11.4	13.1	1.15
		60	9.82	11.3	1.15
Control	0	15	4.75	7.39	1.56
		30	4.36	6.93	1.59
		45	3.87	6.48	1.67
		60	3.82	6.60	1.73
DNP	100	15	0.173	0.309	1.79
		30	0.147	0.287	1.95
		60	0.159	0.312	1.96
		90	0.162	0.327	2.02

Table 4 Concentrations of Dimers at 120°C

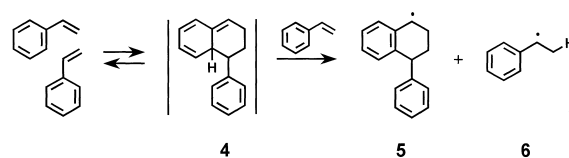
Retarder	Concentration [ppm]	Time [min]	Dimer concentration [ppm]		
			1	2	3
DBS	100	15	92	12	8
		30	197	24	12
		45	299	35	14
		60	402	47	15
	200	15	104	11	23
		30	217	22	32
		45	318	32	40
		60	414	41	46
	1000	15	154	14	466
		30	267	24	540
		45	381	35	662
		60	490	44	796
DNP	100	15	>1	15	>1
		30	>1	28	>1
		60	>1	56	>1
		90	>1	81	9
Control	0	15	>1	14	>1
		30	>1	28	>1
		45	>1	42	>1
		60	3	55	>1

dimers (**1-3**) was examined by GC (Table 4). In the presence of DBS, the concentration of **1** was linearly increased as a function of reaction time. The concentration of **1** reached 400 ppm at 60 min in the presence of 100 ppm DBS. The rate of formation of **1** seemed to increase with increasing DBS concentration. On the other hand, only a trace amount (less than 1 ppm) of **1** was formed in the absence or presence of DNP.

Dimer **3** was also formed only in the presence of DBS. The concentration of **3** significantly increased at a higher concentration of DBS (at 1000 ppm). Dimer **2** was formed regardless of the conditions. These results indicate that the formation of these dimers and the increase of molecular weight of polymer must be associated with the mechanism by which DBS retards polymerization.

### 3. 6. Mechanism of DBS Retardation

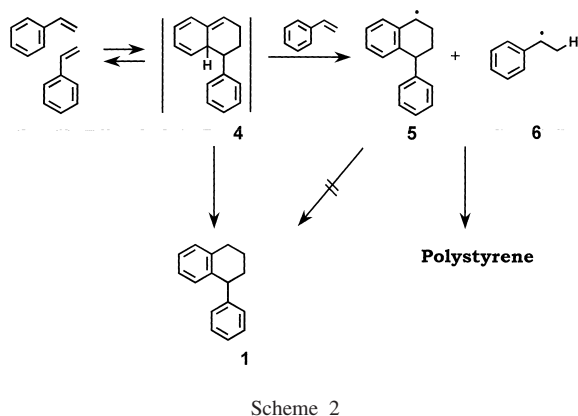
Styrene undergoes self-initiated polymerization even in the absence of initiator. The most widely accepted mechanism for the polymerization of styrene involves an initial [4 + 2] Diels–Alder reaction between two molecules of styrene<sup>11</sup>. The reaction forms the non-aromatized adduct (**4**), which cannot undergo a thermal 1,3-sigmatropic rearrangement due to symmetry considerations and therefore undergoes a molecular-assisted homolytic reaction with another molecule of styrene to form the aromatized radical (**5**) and the radical (**6**) derived from styrene (Scheme 1). Many investigations have been done to elucidate the mechanism<sup>12)–17)</sup>, which is also supported by the isotope effect observed for deuterated styrene<sup>18)</sup>, and the structural analysis of styrene oligomer composed of 6–14 units, prepared by



Scheme 1

thermal polymerization in the presence of ferric chloride as inhibitor. The structural analysis of the oligomers confirmed that the radicals (**5**, **6**) are responsible for initiation<sup>19)</sup>. Strong confirmatory evidence of the mechanism has recently been found in the study of radical polymerization mediated by stable nitroxide<sup>20)</sup>. In the presence of 2,2,6,6-tetramethyl piperidine-1-oxyl, two kinds of alkoxyamine were isolated and characterized to as formed as a result of reaction of initiate radicals (**5**, **6**) with the stable nitroxide.

Generation of **1** in the presence of DBS suggests that DBS may act as a hydrogen donor. Thus the two radicals created by thermal polymerization of styrene abstract hydrogen from DBS to form **1** and ethyl benzene. The sulfonyloxy radical can trap other radicals to form sulfonyl ester. In order to check this possibility, *O*-deuterated DBS (DBS-OD), prepared by the H-D exchange reaction of the acid in D<sub>2</sub>O, was employed as a retarder. <sup>1</sup>H-NMR analysis showed no absence or decrease in hydrogen integration at the 4-position of **1**. Sulfonyloxy radical has high reactivity<sup>21)</sup>, and the radical formed by decomposition of corresponding peroxide is often used as an initiator rather than a retarder. Moreover, if DBS acts as a hydrogen donor, the



molecular weight should be decreased due to the chain transfer mechanism. Therefore, it is unlikely that DBS acts as a chain transfer agent. A more plausible mechanism for the retardation effect of sulfonic acid involves the catalytic action for isomerization of non-aromatized adduct (**4**) to a stable aromatized dimer, such as **1**.

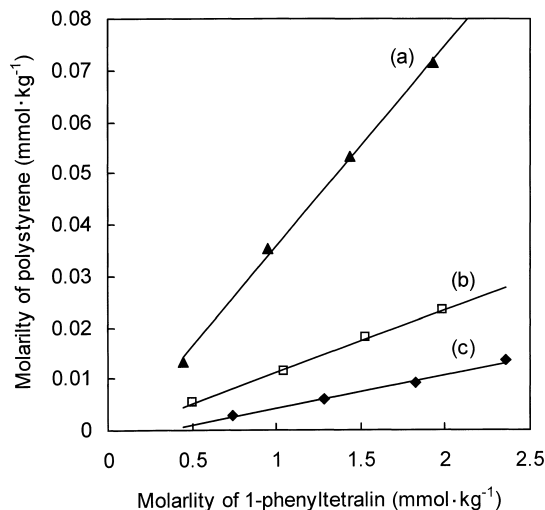
The unstable Diels–Alder adduct (**4**) generating initiate radical **5** and **6** probably undergoes catalyzed isomerization leading to stable compound **1** in the presence of the acid, resulting in decreases in the concentrations of active radicals, **5** and **6** (Scheme 2).

Addition of 0.1% of  $I_2$  retarded the thermal polymerization of styrene and accelerated formation of **1**<sup>11)</sup>. The author suggested that hydrogen iodide was possibly present in the  $I_2$  assisted isomerization of **4**. Although the retardation effect by  $I_2$  was also explained in terms of the free radical mechanism<sup>22,23)</sup>, the formation of **1** and retardation are consistent with the present result with DBS. The formation of **1** in the presence of 2% of *t*-BuOK was also reported<sup>24)</sup>.

The thermal 1,3-sigmatropic rearrangement is impossible for **4**, but would be energetically favorable because this isomerization involves aromatization. The simplest model compound of **4**, 1-methylene-2,4-cyclohexadiene, readily isomerizes to toluene by the addition of proton acid<sup>25,26)</sup>.

If the formation of **1** is closely related with reduction of the amounts of initiator radicals **5** and **6**, the concentrations of **1** and the polymer should be correlated. Figure 4 shows the plot of molar concentration of **1** against that of polymer at different times. The molarity of the polymer was calculated from the average molecular weight shown in Table 3. Although these molecular weights are averaged, the polydispersities ( $M_w/M_n$ ) were low enough to estimate the molarity of the polymer.

In the presence of DBS, the molar concentrations of **1** and polymer had a linear relationship. The molar ratio of polymer/**1** is 0.037 at 100 ppm of DBS. The ratio decreased with increasing DBS concentration



(a) 100 ppm, (b) 200 ppm, (c) 1000 ppm.

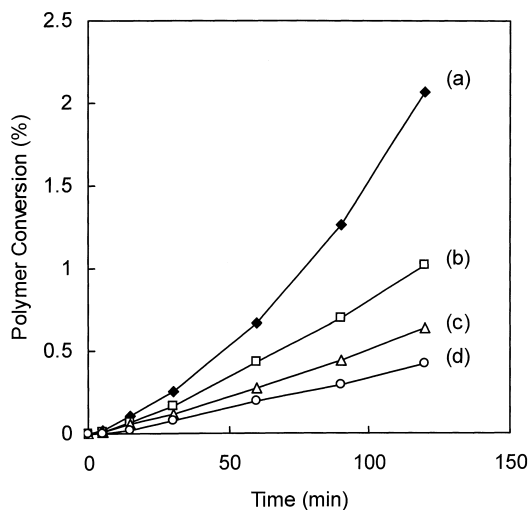
Fig. 4 Plot of Molarity of Polystyrene vs. Molarity of 1-Phenyltetralin in the Presence of DBS

(0.012 at 200 ppm, 0.0065 at 1000 ppm). These results may also support the idea that DBS quenches radical precursor **4** and hence suppresses the polymerization.

However, the concentration of **1** is much higher than the polymer concentration. In the presence of 200 ppm of DBS, the concentration of **1** is about 100 times higher than that of polymer. It is likely that the rate of isomerization of **4** to **1** is considerably faster than that of the molecular-assisted homolytic reaction of **4** to **5**.

The evidence of the molecular weight of the polymer also supports this mechanism. In all cases in the presence of DBS, the amount of polymer was reduced, whereas the molecular weight was increased. This fact also supports the idea that DBS decreases the initiate radicals by acting as an acid catalyst. The retardation effect of DBS is similar to lowering the polymerization temperature. The rate of polymerization decreases with lower polymerization temperature. Therefore, the rate of the thermal Diels–Alder reaction is also reduced by lowering the temperature.

With the increased molecular weight, polydispersity observed in the presence of DBS was lower than that of the unretarded polymer (Table 3). The GPC trace of the unretarded polymer showed pronounced tailing at lower molecular weight (Fig. 3(a)), and decreased with increasing amount of DBS. The disappearance of the polymer component must be the main factor causing the low polydispersity and high molecular weight. Polystyryl radical is known to undergo termination exclusively by coupling. In the proposed mechanism, DBS suppresses generation of initiator radicals so the concentration of polystyryl radical should also be reduced. Thus, the reduced polystyryl radical concen-



◆ = DNBP 100 ppm, □ = + DBS 25 ppm, △ = + DBS 50 ppm, ○ = + DBS 100 ppm.

Fig. 5 Effect of DBS on the Thermal Polymerization of Styrene in the Presence of DNBP

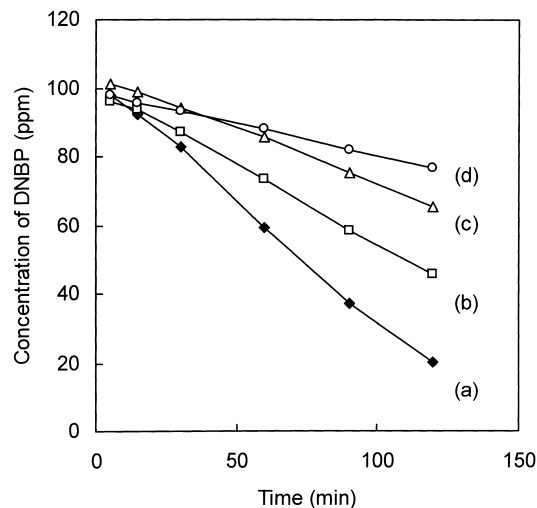
tration may lead to a substantial reduction in the rate of termination. Presumably the reduced polystyryl radical tends to increase continuously before encountering another radical to form the polymer. This might result in the observed high molecular weight and small polydispersity.

The origin of the synergistic effect between DBS and dinitrophenols is interesting. The effect of DBS on the consumption of DNBP in the thermal polymerization was examined.

Various amounts of DBS (0-100 ppm) were added to a styrene solution containing a fixed amount of DNBP (100 ppm) and the polymer conversion and concentration of DNBP were determined periodically. As shown in Fig. 5, the addition of DBS effectively reduced the amount of polymer. For example, the rate of polymerization at 90 min in the absence of DBS was  $2.39 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$  but in the presence of 25 ppm of DBS was  $1.39 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ . The rate of consumption of DNBP was also reduced by addition of DBS (Fig. 6). It is clear that the rate of polymerization and consumption of DNBP were reduced with increasing concentration of DBS.

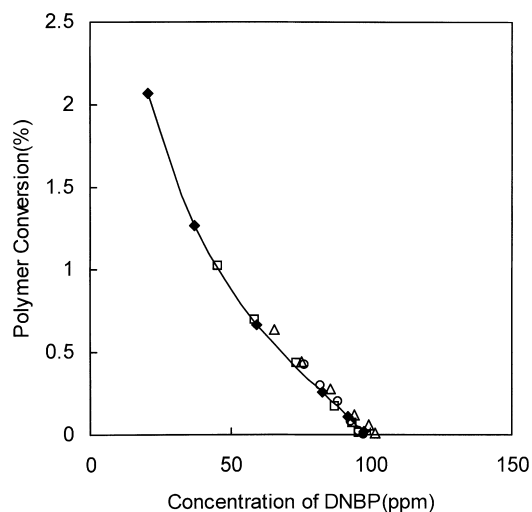
Figure 7 shows the relationship between the polymer conversion and residual DNBP concentration. In the absence of DBS, the polymer conversion was correlated with the DNBP concentration, which reveals that polymer conversion increased with decreased concentration of DNBP (solid line).

Almost all these plots resulting from addition of varying amounts of DBS accord with the result of only DNBP (solid line). Such accordance suggests that addition of DBS does not influence the relationship



◆ = DNBP 100 ppm, □ = + DBS 25 ppm, △ = + DBS 50 ppm, ○ = + DBS 100 ppm.

Fig. 6 Residual Concentration of DNBP in Styrene at 120°C



◆ = DNBP 100 ppm, □ = + DBS 25 ppm, △ = + DBS 50 ppm, ○ = + DBS 100 ppm.

Fig. 7 Relationship of Conversion and Residual DNBP Concentration

between the conversion and DNBP concentration. In other words, DNBP is consumed according to the concentration of the generated radicals. Therefore, the addition of DBS reduces the concentration of initiator radicals.

The significantly small retardation effect of only DBS and the synergistic effect are now clearly explicable, as DBS does not react with the radicals but only suppresses the generation of radicals. The radicals reduced by DBS are efficiently quenched by the co-existing DNBP.

The formation of 1-phenyl-3-methylindane (**3**) and its role in the retardation reaction remains unclear. The drastic change in generation at high concentrations of DBS suggests that formation of **3** is not related to the retardation. The formation of **3** is consistent with the cationic mechanism<sup>11),27),28)</sup>. In the presence of high concentrations of DBS, a small amount of styrene reacts with protons to form a cationic intermediate. The styrene cation reacts with another molecule of styrene and undergoes intramolecular electrophilic aromatic substitution to form **3**.

Since the formation of dimer **2** was independent of conditions, the dimer seems to be formed in the photochemical [2 + 2] cycloaddition<sup>11)</sup>. The formation of dimers leads to monomer loss as well as undesired polymerization if sulfonic acid is used for styrene distillation process. However, this may be not so a big problem because the amount of monomer loss caused by formation of dimer is considerably smaller than that consumed by polystyrene formation. For example, the loss of monomer by formation of polystyrene can be estimated at more than 1 to 2% (10,000 to 20,000 ppm) in the presence of dinitrophenols during 120 min from the result shown in **Fig. 2**. In contrast, the total amount of dimers (**1-3**) was *ca.* 1300 ppm during the 60 min at 120°C (**Table 4**) in the presence of high concentrations of DBS.

#### 4. Conclusion

The present investigation revealed that DBS reduces the initial rate of thermal radical polymerization of styrene. In the presence of DBS, the molecular weight of polystyrene resulting from thermal polymerization was slightly higher than that formed in the absence of DBS. The styrene dimer (**1**), produced by isomerization of the initial Diels–Alder adduct of styrene (**4**), was detected in the thermal polymerization in the presence of DBS. These observations suggest that DBS does not act as a hydrogen donor but behaves as an acid catalyst for the isomerization of **4** to **1**. Thus, the retardation effect can be explained as reduction of the concentration of initiator radicals generated from the molecular-assisted homolysis of **4** and monomeric styrene. The synergistic effect of DBS

and DNBP also suggests this mechanism. Although only DBS cannot be used to replace highly toxic and reactive dinitrophenols, DBS can reduce the amount of dinitrophenols required in the styrene distillation process.

#### References

- 1) Odian, G., "Principles of Polymerization," John Wiley & Sons, New York (1991), p. 259-267.
- 2) Foord, G. S., *J. Chem. Soc.*, 48 (1940).
- 3) Wiley interscience., "Encyclopedia of Polymer Science and Engineering," ed. by Mark, H. F., Vol. 16, John Wiley & Sons, New York (1988), p. 5-21.
- 4) Bagdasar'ian, KH. S., Sinitina, Z. A., *J. Polymer. Sci.*, **52**, 31 (1961).
- 5) Price, C. C., *J. Am. Chem. Soc.*, **65**, 2380 (1943).
- 6) Bartlett, P. D., Kwart, H., *J. Am. Chem. Soc.*, **74**, 3969 (1952).
- 7) Inamoto, N., Simamura, O., *J. Org. Chem.*, **23**, 408 (1957).
- 8) Unpublished observation.
- 9) Kinoshita, M., Miura, Y., *Makromol. Chem.*, **124**, 211 (1969).
- 10) Miura, Y., Kinoshita, M., *Makromol. Chem.*, **160**, 243 (1972).
- 11) Mayo, F. R., *J. Am. Chem. Soc.*, **90**, 1289 (1968).
- 12) Hui, A. W., Hamielec, A. E., *J. Appl. Polym. Sci.*, **16**, 749 (1972).
- 13) Husain, A., Hamielec, A. E., *J. Appl. Polym. Sci.*, **22**, 1207 (1978).
- 14) Graham, W. D., Green, J. G., Pryor, W. A., *J. Org. Chem.*, **44**, 907 (1979).
- 15) Kauffmann, H. F., *Makromol. Chem.*, **180**, 2649 (1979).
- 16) Kauffmann, H. F., *Makromol. Chem.*, **180**, 2665 (1979).
- 17) Kauffmann, H. F., *Makromol. Chem.*, **180**, 2681 (1979).
- 18) Pryor, W. A., Lasswell, L. D., *Adv. Free-Radical Chem.*, **5**, 27 (1975).
- 19) Chong, Y. K., Rizzardo, E., Solomon, D. H., *J. Am. Chem. Soc.*, **105**, 7761 (1983).
- 20) Devonport, W., Michalak, L., Malmström, E., Mate, M., Kurdi, B., Hawker, C. J., Barclay, G. G., Sinta, R., *Macromolecules*, **30**, 1929 (1997).
- 21) Korth, H. G., Neville, A. G., Luszyk, J., *J. Phys. Chem.*, **94**, 8835 (1990).
- 22) Trifan, D. S., Bartlett, P. D., *J. Am. Chem. Soc.*, **81**, 5573 (1959).
- 23) Fraenkel, G., Bartlett, P. D., *J. Am. Chem. Soc.*, **81**, 5582 (1959).
- 24) Zwierzak, A., Pines, H., *J. Org. Chem.*, **28**, 3392 (1963).
- 25) Rozenberg, V. I., Nikanorov, V. A., Salikova, V. I., Bundel', Y. G., Reutov, O. A., *J. Organomet. Chem.*, **102**, 7 (1975).
- 26) Bailey, W. J., Baylouny, R. A., *J. Org. Chem.*, **27**, 3476 (1962).
- 27) Corson, B. B., Dorsky, J., Nickels, J. E., Kutz, W. M., Thayer, H. I., *J. Org. Chem.*, **19**, 17 (1954).
- 28) Spoerri, P. E., Rosen, M. J., *J. Am. Chem. Soc.*, **72**, 4918 (1950).



## 要 旨

## スチレンの熱ラジカル重合に対するスルホン酸の抑制効果

中嶋 淳一<sup>†1), †2)</sup>, 谷崎 青磁<sup>†1)</sup>, 富岡 秀雄<sup>†2)</sup><sup>†1)</sup> 伯東(株)四日市研究所, 510-0007 三重県四日市市別名 6-6-9<sup>†2)</sup> 三重大学工学部分子素材工学科, 514-8507 三重県津市上浜町 1515

スチレン製造プロセスではジニトロフェノール類が重合抑制剤として使用されているが、毒性および自己反応性が高いという問題点を有している。取扱性改善、環境負荷低減の観点からジニトロフェノール類に替わる重合抑制剤の開発が望まれている。重合抑制剤の開発を目的として検討を実施する中で、ドデシルベンゼンスルホン酸 (DBS) がスチレンの熱的ラジカル重合の抑制剤として作用することを見出した。本研究では、DBS の重合抑制機構に関する知見を得るため、DBS 存在下でスチレンのラジカル重合を実施し、発生するポリマー重量の時間変化、平均分子量の測定を行った。その結果、DBS 存在下で生成するポリマーの平均分子量は DBS 無添加時に生成する

ポリマーと比較してわずかに大きくなることが明らかとなった。また、DBS 存在下ではポリマーの生成が抑制されるのに伴って 1-フェニルテトラリン (1) が生成することが分かった。これらの現象から、DBS は開始ラジカルの前駆体である Diels-Alder 付加体 (4) に触媒的に作用して 1 への異性化を促進し、結果として開始ラジカルの発生量を減少させ、重合を抑制することが示唆された。DBS 単独での重合抑制効果はジニトロフェノール類に比べて貧弱であるが、両者を組み合わせることにより、優れた相乗効果を示すことが明らかになり、毒性の高いジニトロフェノール類の使用量を減少できることを見出した。

.....