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Retardation Effect Induced by Pyridine in the Radical Copolymerization of Styrene and Liquid Sulfur Dioxide

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We have found that the radical copolymerization of styrene and liquid sulfur dioxide (liq. SO_2) is retarded when a basic solvent such as pyridine is used; we also investigated the mechanism of the retardation induced by pyridine. The polymerization in pyridine was most strongly retarded when the styrene mole fraction in the feed, $[St]_0/([St]_0+[SO_2]_0)$, was small (below about 0.2) and when the pyridine mole fraction in pyridine-liq.SO_2, $[Py]_0/([Py]_0+[SO_2]_0$, was 0.4—0.5. Moreover, from the results in the reaction of the phenylsulfonyl radical (the model radical for the propagating sulfonyl radical) in pyridine or in a pyridine - liq. SO_2 mixture, it may be concluded that the end unit of the polymer has the pyridinium sulfonate structure ($-SO_3^-HPy^+$) and that the retardation may occur by means of the reaction of the propagating sulfonyl radical with the pyridine-SO_2 complex.

We have been investigating the solvent effect on the compositions of copolymers obtained by the radical copolymerization of styrene and liquid sulfur dioxide (liq. SO_2). The following results have so far been obtained; the copolymer compositions depend on the total monomer concentration and on the nature of the solvent, but hardly on feed composition; that is, the styrene content in the copolymer increases with an increase in the volume fraction of the solvent and by the addition of a basic solvent such as pyridine.[1]

Furthermore, we have found that this polymerization is retarded when a basic solvent such as pyridine, triethylamine, or furan is used.

In this paper, we will dicsuss the mechanism of the retardation induced by pyridine.

Results and Discussion

Retardation of the Radical Copolymerization of Styrene and Liq. SO_2 by Pyridine. In Table 1 the qualitative results are summarized. Table 1 shows that; (1) the polysulfone (methanol-insoluble polymer) is not obtained in pyridine, but is obtained in dichloromethane under the same experimental condition (runs 1 and 2); (2) by increasing the styrene mole fraction in the feed or the azobisisobutyronitrile (AIBN) concentration, polysulfone is obtained, even in pyridine (runs 3, 4, 5, and 6); (3) retardation is also observed in the radical copolymerization of hexene-1 and liq. SO_2 (runs 7 and 8); (4) by the evaporation of the methanol solutions of runs 1, 4, and 5, methanol-soluble (low-molecular weight) styrene polysulfone is obtained.

These results suggest that retardation may occur by the deactivation of the propagating sulfonyl radical (by degradative chain transfer or addition reaction which forms an inactive radical).

Next, we have investigated the rate of copolymerization in pyridine with AIBN under the experimental conditions in which methanol-insoluble polymer was obtained. The styrene mole fraction in the feed and the total concentration of pyridine and liq.SO_2 were kept constant at 0.2 and 12.0 mol/*l* respectively, while the mole fraction of liq.SO_2 in pyridine-liq.SO_2, $[SO_2]_0/([SO_2]_0+[Py]_0)$, was varied from 0.2 to 0.8, using cyclohexane as an inert solvent.[1] The polymerization rates (mol conv./hr) were calculated using both the initial slope of the time-conversion curves and the copolymer compositions, as is shown in Table 2. Rates relative to the rate of run 7 (Table 2) are plotted against $[SO_2]_0/([SO_2]_0+[Py]_0)$ in Fig. 1. From Fig. 1 it is clear that polymerization was most strongly retarded when comparable amounts of pyridine and

TABLE 1. THE QUALITATIVE RESULTS IN RETARDATION BY PYRIDINE[a]

No.	Styrene (m*l*)	SO_2 (m*l*)	Pyridine (m*l*)	Dichloromethane (m*l*)	$\frac{[St]_0}{[St]_0+[SO_2]_0}$[b]	AIBN (g)	Polymer[c] yield (g/hr)
1	6.2	24.0	59.8		0.1	0.1	0/4
2	6.2	24.0		59.8	0.1	0.1	0.13/3
3	18.7	18.7	52.6		0.3	0.1	0.26/2
4	6.6	25.0	47.9		0.1	0.15	0/14.5
5	6.6	25.0	47.9		0.1	0.15	0/21
6	6.6	25.0	47.9		0.1	1.0	3.5/46.5
	Hexene-1 (m*l*)						
7	2.5	7.9	5.0			0.02	0/0.5
8	2.5	7.9		5.0		0.02	1.36/0.5

a) Polymerization temperature, 50°C (No. 1—6), 30°C (No. 7 and 8).
b) Styrene mole fraction in feed.
c) Methanol-insoluble polymer.

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[1] M. Matsuda and M. Iino, *Macromolecules*, **2**, 216 (1969).

TABLE 2. POLYMERIZATION RATES IN PYRIDINE[a)]

No.	Styrene (ml)	SO_2 (ml)	Pyridine (ml)	Cyclo-hexane (ml)	$\frac{[St]_0^{b)}}{[St]_0+[SO_2]_0}$	$\frac{[SO_2]_0^{c)}}{[SO_2]_0+[Py]_0}$	Styrene mol% in copolymer	Rate[d)] (mol%/hr)	Relative rate
1	2.8	4.8	31.1	1.3	0.2	0.2	91.3	0.077	0.48
2	4.1	7.1	27.2	1.6	0.2	0.3	83.0	0.068	0.42
3	5.5	9.5	23.3	1.7	0.2	0.4	73.7	0.040	0.25
4	6.9	11.9	19.4	1.8	0.2	0.5	69.9	0.006	0.04
5	8.3	14.2	15.5	2.0	0.2	0.6	65.3	0.014	0.09
6	9.7	16.6	11.7	2.0	0.2	0.7	66.3	0.089	0.55
7	11.1	19.0	7.8	2.1	0.2	0.8	66.2	0.162	1.00

a) Polymerization temperature 50°C, $[AIBN]_0=1.52\times10^{-3}$ mol/l, total volume 40 ml, $[SO_2]_0+[Py]_0=12.0$ mol/l.
b) Styrene mole fraction in feed.
c) SO_2 mole fraction in pyridine-liq.SO_2.
d) Mol% = [polymer(mole)/charged monomer(styrene + SO_2) (mole)] × 100.

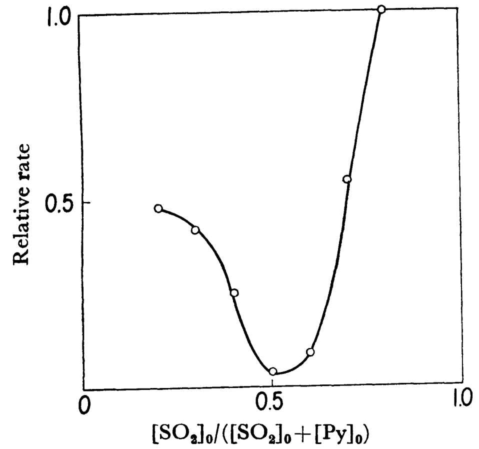

Fig. 1. The plot of relative rate (Table 2) of copolymerization in pyridine against liq. SO_2 mole fraction in liq. SO_2-pyridine, $[SO_2]_0/([SO_2]_0+[Py]_0)$.

liq.SO_2 were present ($[SO_2]_0/([SO_2]_0+[Py]_0)\approx0.5$—0.6) and was less retarded when there was an excess of pyridine.

From this fact we can speculate that retardation may occur as a result of the reaction of the propagating sulfonyl radical and the pyridine-SO_2 complex. It is well known that SO_2 behaves as an electron acceptor and forms charge-transfer complexes with pyridine and various amines. Although it has been reported[2)] that SO_2 forms a 1 : 1 (mole) complex with pyridine, our finding,[3)] obtained by the continuous-variation method in UV spectra, has shown that the complex consists of one mole of pyridine and two moles of SO_2.

Thermal and Photochemical Decompositions of Phenyl Phenylsulfonyl Diimide (PPD) in Pyridine or in a Pyridine-Liq.SO_2 Mixture. To make clear the retardation mechanism speculated as above, we have carried out a model reaction using the phenylsulfonyl radical.

The α-phenylethanesulfonyl radical is better than the phenylsulfonyl radical as a model radical for the propagating sulfonyl radical in the copolymerization of styrene and liq.SO_2, but attempts to prepare it in a solution containing pyridine were unsuccessful.

As the source of the phenylsulfonyl radical, we have used phenyl phenylsulfonyl diimide (PPD), which has been reported by Rosenthal and Overberger[4)] to form this radical by thermal decomposition. Phenylsulfonyl halide was inadequate because of its ionic reaction with pyridine.

The results obtained are summarized in Table 3. Table 3 shows that pyridinium benzenesulfonate ($PhSO_3^-HPy^+$,PBS) was obtained in a good yield in the reaction in the pyridine-liq.SO_2 mixture; on the other hand, in pyridine this product was not obtained. PBS is water-soluble and was obtained from the water-soluble part of the reaction mixture, as will be described in the Experimental section. From the ether-soluble part, we obtained azobenzene; its yield was best in the reaction in pyridine. We could not identify

TABLE 3. THERMAL DECOMPOSITION OF PHENYL PHENYLSULFONYL DIIMIDE (PPD)[a)]

PPD g(mole)	SO_2 (ml)	Pyridine (ml)	$\frac{[SO_2]_0^{b)}}{[SO_2]_0+[Py]_0}$	PBS[c)] g(mole%)	Product Azobenzene g(mol%)	N_2 (mol%)
9.84(0.04)	0.0	50.0	0.0	0.0[d)]	0.30(4.1)	
9.84(0.04)	0.0	80.0	0.0	0.0[d)]	0.39(5.4)	53
9.84(0.04)	8.4	51.6	0.2	5.54(58.4)	0.03(0.4)	99
9.84(0.04)	23.7	36.3	0.5	5.20(54.8)	0.03(0.4)	87
9.84(0.04)	43.4	16.6	0.8	2.87(30.2)	0.06(0.8)	95

a) 70°C, 24 hr.
b) SO_2 mole fraction in pyridine —liq.SO_2.
c) Pyridinium benzene sulfonate, mole% based on PPD.
d) About 0.8 g of water-soluble product (unidentified) was obtained.

[2)] A. Tramer, *Bull. Acad. Polon. Sci.*, **5**, 501 (1957).

[3)] M. Matsuda and T. Hirayama, *J. Polym. Sci.*, **5**, 2769 (1967).

[4)] A. J. Rosenthal and C. G. Overberger, *J. Amer. Chem. Soc.*, **82**, 108 (1960).

Table 4. Photo-chemical decomposition of phenyl phenylsulfonyl diimide (PPD)[a)]

	PPD g(mol)	SO_2 (m*l*)	Pyridine (m*l*)	$\frac{[SO_2]_0^{b)}}{[SO_2]_0+[Py]_0}$	PBS[c)] g(mol%)	N_2 (mol%)
Irradiation	4.92(0.02)	11.8	18.2	0.5	1.49(31.4)	96
Dark	4.92(0.02)	11.8	18.2	0.5		0.0

a) Room temperature, 36 hr.
b) SO_2 mole fraction in pyridine-liq.SO_2.
c) Pyridinium benzene sulfonate, mol% based on PPD.

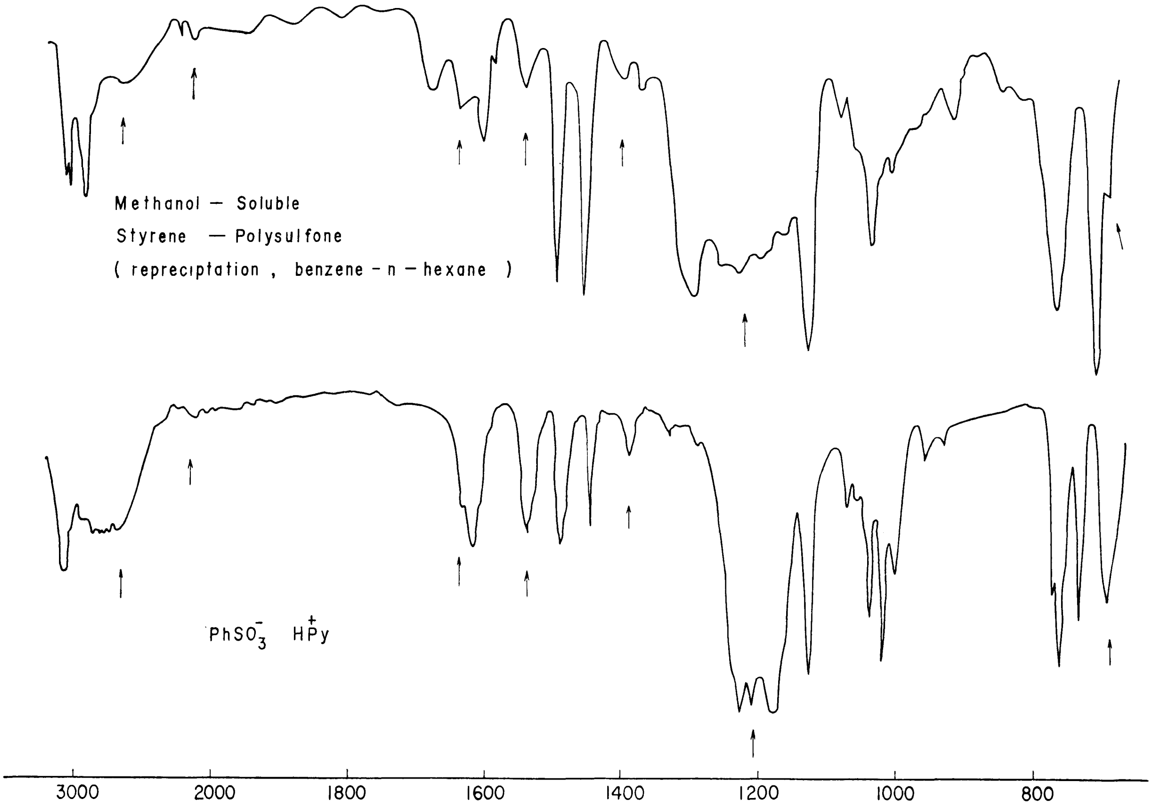

Fig. 2. IR spectra of methanol-soluble styrene-polysulfone obtained by copolymerization in pyridine and $PhSO_3^-$ HPy^+.

any product other than azobenzene from the ether-soluble part.

Table 4 shows that the photolysis of PPD at room temperature in the pyridine-liq.SO_2 mixture gave PBS, while in the dark the reaction did not occur. It is well known that an azo-compound such as PPD is subject to homolysis by light and forms two radicals and nitrogen. Therefore, the results in Table 3 indicate that PBS arises from the phenylsulfonyl radical.

The infrared spectra of methanol-soluble styrene polysulfone described in the preceeding section and PBS are shown in Fig. 2. The arrow in the spectra of polysulfone indicates a peak which does not exist in ordinary styrene polysulfone obtained in bulk or in a non-basic solvent. It is clear that these peaks arise from the end unit of this polymer, formed by termination. The peak at 2200 cm^{-1} indicates the presence of the moiety of the initiator (AIBN) as another end unit of this polymer. All the peaks denoted by arrows also exist in the spectra of PBS. This fact indicates that the end unit of this polymer has a structure similar to that of PBS, namely, $-SO_3^-HPy^+$. In fact, the aqueous solution of this polymer (it is dissolved for the most part in water) is acidic, as is PBS. From the above results, it seems certain that retardation occurs by the deactivation of the propagating sulfonyl radical and that pyridinium sulfonate is formed ultimately. Moreover, the fact that PBS is obtained in a pyridine-liq.SO_2 mixture, but not in pyridine, suggests that the propagating sulfonyl radical is deactivated by the reaction with the pyridine-SO_2 complex.

The results in the thermal decompositions of phenyl *p*-methylphenylsulfonyl diimide (*p*-methylPPD) and phenyl *p*-chlorophenylsulfonyl diimide (*p*-chloroPPD) are summarized in Table 5. In *p*-methylPPD, though the yield was low, pyridinium *p*-toluenesulfonate (*p*-methylPBS) was obtained in the reaction in pyridine. Its formation may be considered to be due to the reaction of pyridine and *p*-toluenesulfinic acid, which is itself formed by the following hydrogen abstraction reaction, because *p*-methylPPD has very reactive hydrogen atoms (a methyl group attached to a phenyl group) toward abstraction, while PPD and *p*-chloroPPD, in which no pyridinium sulfonates were obtained in pyridine, have no such hydrogen atoms;

$$CH_3C_6H_4SO_2\cdot + CH_3C_6H_4SO_2N_2C_6H_5 \longrightarrow$$
$$CH_3C_6H_4SO_2H + \cdot CH_2C_6H_4SO_2N_2C_6H_5$$

TABLE 5. THERMAL DECOMPOSITION OF PHENYL *p*-METHYLPHENYLSULFONYL DIIMIDE (*p*-METHYL PPD) OR PHENYL *p*-CHLOROPHENYLSULFONYL DIIMIDE (*p*-CHLORO PPD)[a]

SO_2 (m*l*)	Pyridine (m*l*)	$\frac{[SO_2]_0}{[SO_2]_0+[Py]_0}$[b]	*p*-MethylPPD g(mol)	*p*-MethylPBS[c] (g)	N_2 (mol%)[d]	*p*-ChloroPPD g(mol)	*p*-ChloroPBS +PBS (g)	N_2 (mol%)
0.0	30.0	0.0	5.20(0.02)	0.26	57	5.61(0.02)	0.0	79
4.2	25.8	0.2	5.20(0.02)	1.34	99	5.61(0.02)	0.67	97
11.8	18.2	0.5	5.20(0.02)	1.79	82	5.61(0.02)	1.10	74
21.7	8.3	0.8	5.20(0.02)	0.71	70	5.61(0.02)		86

a) 70°C, 24 hr. b) SO_2 mole fraction in pyridine-liq.SO_2.
c) It includes a small amount of PBS (from its NMR spectra). d) Based on diimide.

In fact, we have carried out the reaction of benzene sulfinic acid with pyridine and obtained PBS, as will be described in the Experimental section. In *p*-chloro-PPD, pyridinium *p*-chlorobenzenesulfonate (*p*-chloro-PBS) and PBS were obtained in the pyridine-liq.SO_2 mixture, but not in pyridine. PBS probably arises from the phenylsulfonyl radical formed by the addition reaction of the phenyl radical and SO_2. These results also support the idea that the sulfonyl radical is deactivated by the reaction with the pyridine-SO_2 complex.

We can suggest the following two mechanisms as possible for the deactivation of the sulfonyl radical;

$$(1)\quad \sim SO_2\cdot + \text{complex} \longrightarrow$$
$$\sim SO_2H + \text{inactive radical} \xrightarrow{+Py}$$
$$\sim SO_3^{-}HPy^{+}$$

$$(2)\quad \sim SO_2\cdot + \text{complex} \longrightarrow$$
$$\sim SO_2 - \text{complex}\cdot(\text{inactive radical}) \longrightarrow$$
$$\sim SO_3^{-}HPy^{+}$$

It is well known that when a radical attacks an aromatic ring, an addition reaction (mechanism 2) usually occurs, but not hydrogen abstraction reaction (substitution reaction on hydrogen, mechanism 1).[5] Accordingly, it seems reasonable to consider that retardation occurs by the addition reaction of the sulfonyl radical to the complex and the formation of an inactive (stable) radical (mechanism 2).

Experimental

Materials. Styrene, AIBN, pyridine, dichloromethane, and cyclohexane were purified by the usual method. Liq. SO_2 was dehydrated by phosphorus pentoxide and distilled *in vacuo*. PPD was prepared[6] from sodium benzenesulfinate and benzenediazonium chloride and was recrystallized from ethanol (mp 74—76°C; lit,[6] 78°C). *p*-MethylPPD and *p*-chloroPPD were prepared using the same method (*p*-methyl PPD: mp 93—95°C; lit,[7] 95°C, *p*-chloroPPD: mp 102—103°C; lit,[6] 106°C).

Copolymerization of Styrene and Liq.SO_2. Polymerization was carried out using a method previously reported.[8] The polymerization rates were measured by the gravimetric method, and the copolymer compositions were determined from the elementary analyses of carbon.

Thermal Decomposition of PPD in Pyridine or in a Pyridine-Liq.SO_2 Mixture. 9.84 g (0.04 mol) of PPD were reacted at 70°C for 24 hr in pyridine (50 or 80 m*l*) or in a pyridine-liq.SO_2 mixture. The mole fraction of liq.SO_2 in the pyridine-liq.SO_2 mixture was varied from 0.2 to 0.8 (pyridine +liq.SO_2=60 m*l*; Table 3). After the reaction the liq.SO_2 was evaporated and the pyridine was distilled off under reduced pressure (1—2 mmHg). The residue thus obtained was extracted with water and ether. In the case of the reaction in the pyridine-liq.SO_2 mixture, the evaporation of the water of the water layer and recrystallization from acetone gave PBS (2.9—5.5 g; Table 3): hygroscopic, mp 129.5—132°C; lit,[9] 125—130°C. Its IR and NMR spectra coincided with those of an authentic sample prepared from benzene sulfonic acid and pyridine. PBS could also be obtained by extraction with dehydrated acetone instead of water. This fact indicates that PBS is not formed by the addition of water. On the other hand, in the case of the reaction in pyridine, the evaporation of the water from the water layer gave no PBS, but did give an unidentified product in only a small yield (0.8 g): nonhygroscopic, mp 200—202°C. In either pyridine-liq.SO_2 or pyridine systems, the ether layer was chromatographed on a silica gel column; subsequent elution with a petroleum ether-benzene mixture gave azobenzene in a yield such as is shown in Table 3: mp 65—68°C, identified by comparison with an authentic sample.

In *p*-methylPPD, *p*-methylPBS was identified by comparison with an authentic sample: hygroscopic, mp 117—123°C (recrystallized from acetone); lit,[10] 119—121°C. In the case of *p*-chloroPPD, the IR spectrum of the product shows, when compares with that of authentic *p*-chloroPBS, that a mixture of *p*-chloroPBS and PBS was obtained.

Photo-decomposition of PPD. The reactants in a quartz-reaction vessel were irradiated at room temperature by means of a high-pressure mercury lamp about 5 cm from the vessel.

The Reaction of Benzenesulfinic Acid with Pyridine. 5.26 g (0.03 mol) of benzenesulfinic acid and pyridine (30 m*l*) were reacted at 70°C for 24 hr. By the same procedure as in the case of PPD, 1.38 g (19.3%) of PBS were thus obtained. 0.3 g of PBS was also obtained in the reaction in the pyridine—liq.SO_2 mixture (mole ratio 1:1) instaed of in pyridine.

Measurement of the Nitrogen Volume Evolved. The volume of the nitrogen evolved was measured from the difference in the volumes at 20°C and 1 atm before and after the reaction, using a mercury manometer. The reaction vessel was filled with nitrogen at 1 atm and 20°C prior to the reaction. In the measurement, the reaction vessel was cooled by liquid nitrogen to prevent any effect of the liq.SO_2.

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5) W. A. Pryor, "Free Radicals," McGraw-Hill Book Company, New York (1966), Chap. 16.

6) A. Hantzsch and M. Singer, *Ber.*, **30**, 312 (1897), **31**, 641 (1898).

7) P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921).

8) N. Tokura and M. Matsuda, *Kogyo Kagaku Zasshi*, **64**, 501 (1961).

9) L. Field, *J. Amer. Chem. Soc.*, **74**, 394 (1952).

10) W. E. Rosen, *J. Org. Chem.*, **26**, 5190 (1961).