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Sulfinic Acid Derivatives as Accelerators in the Polymerization of Methyl Methacrylate

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INTRODUCTION

The use of organic sulfinic acids to promote rapid polymerization of methyl methacrylate and other vinyl monomers has been advocated for a number of reasons, one of which was to decrease the color of the polymeric product.[1-9] This is a big advantage over the colored products that are usually formed when methyl methacrylate is polymerized with a benzoyl peroxide–amine system. Furthermore, sulfinic acid shows no induction period. The polymerization starts immediately, even when hydroquinone-stabilized monomer is used. The sulfinic acid does not oxidize the hydroquinone inhibitor or react with any quinone present. In the presence of air, sulfinic acids readily oxidize to sulfonic acids and other oxidation products which do not act as polymerization activators. This poor storage stability limits the use of these accelerators.

Recently, Bredereck and Bäder[10-11] have synthesized derivatives of sulfinic acid, such as oxysulfones, α-aminosulfones, and sulfinic acid salts. Some of these compounds had good storage stability and were efficient accelerators for the polymerization of monomer-polymer mixtures at room temperature.[12-13] In the present investigation, a more detailed study of the use of the amine salts of *p*-toluenesulfinic acid as possible accelerators in the polymerization of methyl methacrylate was undertaken.

EXPERIMENTAL PROCEDURE AND RESULTS

Synthesis

The sodium salt of *p*-toluenesulfinic acid (Eastman reagent grade) was converted to the acid. The free acid was dissolved in ether solution according to the method suggested by Bredereck[10] and an ether solution of a very slight excess of the respective amine was added. If a salt crystallized out, it was filtered off. Sometimes, on partial evaporation of the solution, an oily layer separated. This oil was removed and extracted with ether. If the material did not crystallize, the remaining solvent was removed at room temperature at approximately 60 mm. pressure. The material was then heated to 60°C. at 2 to 4 mm. pressure, cooled and stored at 2 to 4°C. until crystallization occurred. The yield of impure solid or oil was nearly quantitative.

TABLE I

PROPERTIES OF AMINE SALTS OF *p*-TOLUENESULFINIC ACID

Amine	Melting point, °C. Found	Melting point, °C. Reported	Composition,[e] % Found		Calcd.	
Aliphatic						
di-*n*-propyl	60	—	S = 12.1	N = 5.4	S = 12.4	N = 5.4
di-*n*-butyl	105	104–106	—	—	—	—
diisobutyl[a]	120	—	C = 59.7	H = 9.1	C = 60.1	H = 9.0[b]
di-*sec*-butyl	Oil	—	—	—	—	—
di-*n*-hexyl	119	119	—	—	—	—
dicyclohexyl[c]	153	—	C = 67.5	H = 9.3	C = 67.5	H = 9.2
N-methylcyclohexyl[a]	138	—	C = 58.7 N = 4.9	H = 8.0	C = 58.9 N = 4.9	H = 8.1[b]
diethanol	Oil	—	—	—	—	—
tri-*n*-butyl	Oil	40–43	—	—	—	—
tri-*n*-hexyl	Oil	—	—	—	—	—
N,*N*-diethylcyclohexyl[a]	100	—	C = 62.5	H = 8.7	C = 61.9	H = 8.8[b]
Aromatic						
aniline	116	118	—	—	—	—
N-methylaniline	Oil	—	—	—	—	—
m-toluidine	117	120	C = 63.4 N = 5.2	H = 6.5	C = 63.8 N = 5.3	H = 6.5
dimethyl-*p*-toluidine	Oil	—	—	—	—	—
dibenzylamine	132[d]	—	C = 70.8 N = 4.0	H = 6.6	C = 71.2 N = 4.0	H = 6.5
dimethyl-α-naphthylamine	Oil	—	—	—	—	—
phenylhydrazine	158	158	—	—	—	—

Heterocyclic						
pyridine	Oil[e]	—	—	—	—	—
morpholine	124–125	—	C = 54.1	H = 7.1	C = 54.3	H = 7.0
piperidine[a]	130	130	C = 56.1	H = 7.4	C = 55.9	H = 7.4[b]
pyrrole	Solid[f]	—	—	—	—	—
pyrrolidine	Oil	—	—	—	—	—

[a] Sulfonic acid salt.

[b] Calculated for sulfonic acid salt.

[c] On recrystallization oxidized to the sulfonic acid salt. M.p. = 179°C. Composition (%), C = 64.0, H = 8.7 (found); C = 64.5, H = 8.7 (calcd.).

[d] On recrystallization oxidized to the sulfonic acid salt. M.p. = 162°C. Composition (%), S = 7.7, N = 3.8 (found); S = 7.7, N = 3.7(calcd.).

[e] Oxidized to hygroscopic solid.

[f] No sharp melting point.

[g] Analyses were performed by R. A. Paulson of the Analytical Chemistry Section of the National Bureau of Standards. Experimental results are the average of two determinations.

Solids were purified by repeated recrystallization, usually from ether to which small quantities of methanol had been added. Recrystallization was continued until a colorless crystalline material with a sharp melting point was obtained. Those compounds that had been reported in the literature were identified by their melting points. The composition of all other solids was determined by analysis for carbon, hydrogen, sulfur, or nitrogen. Considerable difficulty was encountered in purifying oily products, which had high boiling points, even in high vacuum. These compounds were tested for their accelerator efficiency without further purification.

Table I gives the melting points obtained in this study and those found in the literature. Analyses of the crystalline compounds not previously reported are also given. It will be seen that most salts of tertiary amines are oils. Salts of most primary and many secondary aliphatic amines are solids. The *p*-toluenesulfinic acid salts of diisobutylamine, *N*-methylcyclohexylamine, *N*,*N*-diethylcyclohexylamine, and piperidine were unstable in ether solution and the corresponding sulfonic acids crystallized on standing. On repeated recrystallization, the dicyclohexyl and dibenzylamines also oxidized to the sulfonic acid.

Polymerization

The effectiveness of these salts as accelerators of the peroxide-catalyzed polymerization of methyl methacrylate was determined. Monomer containing 2% benzoyl peroxide and 0.006% hydroquinone inhibitor was prepared and varying concentrations of sulfinic acids were added. The polymerization reaction at 37°C. was followed by means of an Ultra-Viscoson ultrasonic viscosity apparatus in the manner previously reported.[14]

Results of the polymerization studies are given in Table II and Figure 1. The salts of the aromatic amines are the most efficient accelerators encountered in this study. In the presence of *N*-methylaniline salt, a 1000 cp.g./cm.^{3} value was reached in less than 12 minutes. In comparison, the time necessary to reach 1000 cp.g./cm.^{3} for the commercially used benzoyl peroxide–di(β-hydroxyethyl)-*m*-toluidine and benzoyl peroxide–dimethyl-*p*-toluidine systems as determined in a previous study were 21 and 36 minutes, respectively. Salts of naphthylamines showed a much reduced activity. The polymerization products of all aromatic amines were yellowish or red. It may be possible to decrease somewhat the color of these products by careful purification of the raw materials and possibly by distillation of the amine salts in a molecular still. In agreement with Bredereck,[10] it was found that the storage stability of the aromatic amines was much better than that of the free *p*-toluenesulfinic acid. The *N*-methylaniline salt showed no decrease in activity after storage for 5 months. The crystalline *m*-toluidine salt showed a faint yellow color within 10 months.

Salts of aliphatic amines showed a much decreased activity. The oily tertiary amine salts were somewhat faster acting than the crystalline secondary amines. Tri-*n*-hexylamine appeared to be the best accelerator in this series. Increase in chain length of the hydrocarbon radical decreased the accelerating activity. The isomeric di-*n*-butyl and diisobutylamines had approximately the same accelerating efficiency. The di-*sec*-butylamine was a less effective accelerator. Amines of cyclic hydrocarbons such as dicyclohexylamine are only slightly soluble in monomer and do not accelerate the polymerization appreciably. Salts of heterocyclic amines show only slightly improved accelerating efficiency as compared to the aliphatic amine salts.

Bredereck, in his paper,[12] shows the high efficiency of α-oxy and α-amino sulfones. He reported that the latter compound is stable in air. Derivatives of *p*-toluenesulfinic acid were prepared according to his directions.[10] Monomer containing 2% of the *p*-tolyl oxymethylsulfone or *N*-ethylbis(*p*-tolylsulfonemethyl)amine and 2% benzoyl peroxide polymerized rather slowly. After 1 hour, the solutions showed a viscosity of 6.5 and 24 cp.g./cm.,[3] respectively.

Phosphinic acids have also been suggested as accelerators and their use has been patented by Loritsch.[15] The di-*n*-propylamine and methylaniline salts of phenylphosphinic acid were prepared by methods similar to those used for sulfinic acid salts. The salts are oily liquids. The di-*n*-propylamine salt gave an analysis of C = 59.1%, H = 9.2% (calculated values C = 59.2%, H = 9.0%). Neither phenylphosphinic acid nor its di-*n*-propylamine or methylaniline salts showed any appreciable effects on

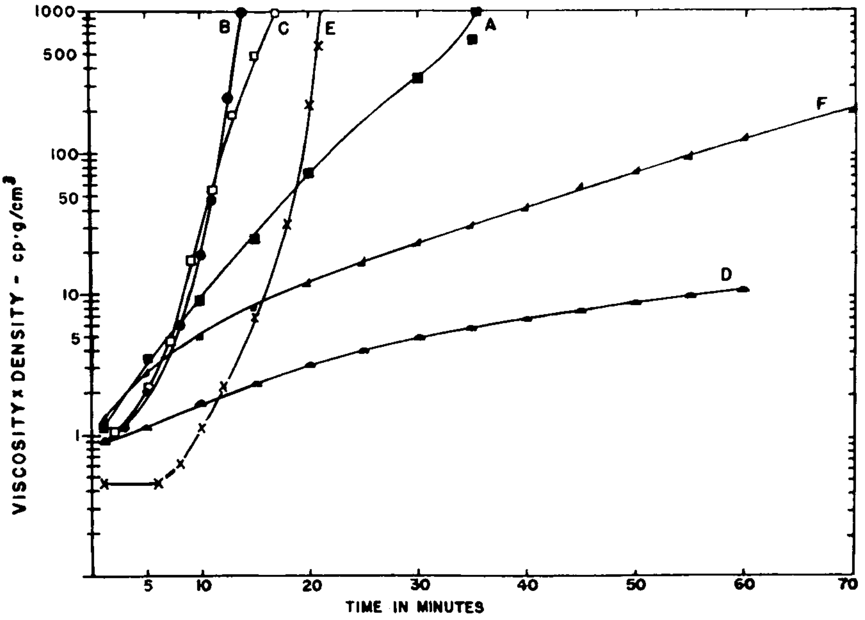

Fig. 1. Polymerization of methyl methacrylate in the presence of *p*-toluenesulfinic acid-amine salts at 37 °C. and 2% benzoyl peroxide concentration. A = aniline salt: 1%. B = methylaniline salt: 1%. C = dimethyl-*p*-toluidine salt: 2%. D = di-n-butylamine salt: 2%. E = di(β-hydroxyethyl)-*m*-toluidine: 1%. F = *p*-toluenesulfinic acid: 2%.

TABLE II

Accelerators of the Polymerization of Methyl Methacrylate Amine Salts of *p*-Toluenesulfinic Acid

Benzoyl peroxide concentration, 2%

Amine salt	Soly. in monomer	Concn., %	Time, min.	Viscosity[a] × density, cp. × g./cm.^{3}	Polymer color
Aliphatic					
di-*n*-propyl	s.	2.0	60	10	Faint yellow
		2.0	163	1000	
di-*n*-butyl	sl.s.	<2.0	60	12	Colorless
		0.5	60	19	
		0.05	60	1	
diisobutyl	sl.s.	<2.0	60	18	Slight yellow
di-*sec*-butyl	s.	2.0	60	1.5	Yellow
di-*n*-hexyl	sl.s.	<2.0	60	9	Colorless
		0.2	60	No change	
dicyclohexyl	sl.s.	<0.5	60	No change	Colorless
N-methylcyclohexyl	ins.	<0.2	60	No change	Colorless
diethanol	ins.	<2.0	60	No change	Colorless
tri-*n*-butyl	s.	2.0	60	5	Faint yellow
tri-*n*-hexyl	s.	2.0	60	105	Colorless
		2.0	101	1000	
		1.0	60	50	
N,*N*-diethylcyclohexyl	s.	2.0	60	8	Slight yellow

Aromatic					
aniline	s.	2.0	36	3600	Yellowish red
		0.5	116	1000	
N-methylaniline	s.	2.0	12	1300	Reddish yellow
		1.0	14	1000	
		0.5	60	72	
m-toluidine	s.	2.0	28	1000	Reddish brown
		0.5	60	475	
dimethyl-*p*-toluidine	s.	2.0	17	1000	Brownish yellow
dibenzylamine	sl. s.	<0.5	60	6	Colorless
dimethyl-α-naphthylamine	ins.	<0.5	60	No change	Reddish orange
phenylhydrazine	sl. s.	<2.0	60	21	Yellow
		0.2	60	11	
Heterocyclic					
pyridine	s.	2.0	60	13.3	Colorless
morpholine	ins.	<2.0	60	28	Colorless
		0.2	60	No change	
pyrrolidine	s.	2.0	60	24	Colorless
piperidine	s.	2.0	60	12	Colorless
Other accelerators (not amine salts)					
p-toluenesulfinic acid	s.	2.0	130	1000	Colorless
		1.0	205	1000	
di(β-hydroxyethyl)-*m*-toluidine	s.	1.0	19	1000	Yellow
dimethyl-*p*-toluidine	s.	2.0	185	1000	Yellow
		0.5	34	1000	

[a] Values are not corrected for rise in temperature due to the exothermic polymerization reaction. It is also assumed that the modulus of rigidity of the solution is negligible in comparison to the coefficient of viscosity.

TABLE III

SETTING TIME AND PHYSICAL PROPERTIES OF MONOMER–POLYMER SLURRIES

(Mixture: 1 g. ground polymer containing 1% benzoyl peroxide and 1 ml. of hydroquinone-stabilized monomer)

Expt. No.	Additives in Monomer	Setting time, min.	Indentation,[a] mm.			Recovery,[a] %		
			30-min.	1-hr.	5 days	30-min.	1-hr.	5 days
1	2% A[b]	6–8	0.24	0.15	0.10	29	46	73
2	2% B[c]	>30	—	—	—	—	—	—
3	Same as 2 + 16% methanol	13	—	—	Soft	—	—	Soft
4	Same as 2 + 30% methanol	8	—	—	Soft	—	—	Soft
5	2% C[d]	8–9	—	Soft	0.24	—	Soft	26
6	4% C + 3% benzoyl peroxide	6–7	—	0.25	0.17	—	16	49
7	Same as 6 + 6% methanol	—	—	0.26	0.15	—	12	54
8	Same as 6 + 16% methanol	7	—	0.17	0.13	—	49	68
9	Same as 8 + 1 drop 30% H_2O_2	7	—	Soft	0.20	—	Soft	65
10	Same as 8 + 1 drop 3% H_2O_2	7	—	—	—	—	—	—
11	4% C + 4% *tert*-butyl hydroperoxide + 16% methanol	7	—	0.23	0.12	—	30	63
12	Same as 11 + 2 drops 30% H_2O_2	—	—	Soft	0.27	—	Soft	2
13	Same as 11 + 1 drop 3% H_2O_2	7	—	0.19	0.14	—	41	66
14	2% D[e]	>30	—	—	—	—	—	—
15	2% D + 2% benzoyl peroxide	>30	—	—	—	—	—	—
16	Same as 15 + 16% methanol + 1 drop H_2O_2	24	—	—	—	—	—	—
17	2% di(β-hydroxyethyl)-*m*-toluidine	9	—	0.13	0.10	—	46	78
18	2% dimethyl-*p*-toluidine	7	0.18	0.13	0.09	39	52	79
19	1% dimethyl-*p*-toluidine	9	0.23	0.15	0.10	36	48	76

[a] Average of two or more specimens.
[b] A = *N*-methylaniline salt of *p*-toluenesulfinic acid.
[c] B = di-*n*-hexylamine salt of *p*-toluenesulfinic acid.
[d] C = *N*-ethylbis(*p*-tolylsulfonemethyl)amine.
[e] D = *p*-tolyl oxymethylsulfone.

the polymerization rate. Use of a hydroperoxide such as *tert*-butyl hydroperoxide instead of benzoyl peroxide as suggested by Loritsch did not decrease the setting time.

Hardening of Monomer–Polymer Mixtures

The setting time of monomer–polymer mixtures containing various amines, was determined by a modification of the A. S. T. M. penetration test for bituminous materials.[16]

One gram of ground polymer powder containing 1% benzoyl peroxide was mixed with 1 ml. of 0.006% hydroquinone-inhibited monomer containing the various amine salts. Additional peroxide, methanol, or hydrogen peroxide were also added to the monomer. The mix was placed on a glass plate in a brass ring 0.5 cm. high and 1.1 cm. in diameter. Polyethylene, a glass plate and 100 g. weight were placed on top of the ring for 2.5 minutes. The ring was then placed in a 37°C. air bath. A needle, attached to the dial gage and under 100 g. load, was lowered into the center of the ring at 3 minutes from the start of mix and left for 5 seconds before a reading was taken. Readings were repeated every minute until the material could no longer be penetrated.

It will be seen in Table III that mixtures containing the methylaniline salt as well as the *N*-ethylbis(*p*-tolylsulfonemethyl)amine showed a very short setting time. The mixture hardened much slower when di-*n*-hexylamine salt was used as accelerator. Under the experimental condition, no appreciable decrease in setting time on addition of methanol or a trace of hydrogen peroxide as reported by Bredereck[12] was observed. The preparation of the polymer, particle size, and the exact monomer–polymer ratio that was employed are not given. In the absence of more complete data, it is not possible to explain these variations in setting time. Bredereck followed the course of the polymerization by the rise in temperature only. Thus, his results do not make it possible to draw any conclusions concerning the physical properties of the polymeric products formed.

In order to obtain information on the physical characteristics such as hardness and elastic properties of the polymerized materials, their indentation and recovery were measured using the Rockwell superficial hardness tester.[17] Results of the indentation tests and per cent recovery are given in Table III. Polymers prepared with the methylaniline salt of *p*-toluenesulfinic acid showed low indentation values and high per cent recovery. These polymers have physical characteristics similar to those of materials polymerized with amine accelerators such as di(β-hydroxyethyl)-*m*-toluidine or dimethyl-*p*-toluidine. The salt of tri-*n*-hexylamine sets much more slowly. Addition of methanol considerably decreased the setting time. The resulting polymer was too soft for most applications. *N*-Ethylbis(*p*-tolylsulfonemethyl)amine also produced a softer material. Indentation and hardness were improved somewhat by the addition of 16% methanol and a little hydrogen peroxide. Substituting *tert*-butyl hydroperoxide for a portion of the benzoyl peroxide catalyst brought about a slight improvement of physical properties.

References

1. Hagger, O., *Helv. Chim. Acta* **31**, 1624 (1948).

2. *Ibid.* **34**, 1872 (1951).

3. Castan, P., and Hagger, O., U. S. Patent 2,567,803, Sept. 11, 1951 (to Gebr. deTrey); Swiss Patent 255,978, Feb. 1, 1949.

4. Imperial Chemical Industries Ltd., Brit. Patent 586,796, April 1, 1947.

5. Farbwerke Hoechst, German Patent 861,156, December 29, 1952.

6. Ynfiesta, J. L., Yanes, J. F., and Sanchez, F. R., *Anales real soc. espan fis y. quim.* **47B**, 53 (1951).

7. Hashihama, Y., Sumitomo, H., and Okabe, J., *J. Chem. Soc. Japan, Ind. Chem. Sec.* **56**, 25 (1953).

8. Taylor, P. B., and Frank, S. L., *J. Dental Res.* **29**, 486 (1950).

9. Schroder, A., and Santorik, St., *Schweizerische Monatszeitschrift für Zahnheilkunde* **60**, 937 (1950).

10. Bredereck, H., and Bäder, E., *Chem. Ber.* **87**, 129 (1954).

11. Bäder, E., and Hermann, H. D., *Chem. Ber.* **88**, 41 (1955).

12. Bredereck, H., Bäder, E., and Wohnhas, A., *Makromol. Chem.* **12**, 100 (1954).

13. W. C. Heraeus G. M. B. H. and Deutsche Gold und Silberscheideanstalt vorm. Roessler, Brit Patents 710,534 and 710,535, June 16, 1954; British Patent 708,077, April 28, 1954; German Patent 913,477, June 14, 1954; and German Patent 916,733, August 16, 1954.

14. Davenport, R. M., and Brauer, G. M. (manuscript in preparation).

15. Loritsch, J. A., U. S. Patent 2,543,635, February 27, 1951.

16. American Society for Testing Materials. Standard method of test for penetration for bituminous materials. A.S.T.M. Designation D-5-52. A. S. T. M. Standards on Bituminous Materials for Highway Construction, Waterproofing and Roofing.

17. Sweeney, W. T., Sheehan, W. D., and Yost, E. L., *J. Am. Dent. Ass.* **49**, 513 (1954).

Synopsis

A study was made of the efficiency of amine salts of *p*-toluenesulfinic acid as accelerators in the polymerization of methyl methacrylate. These compounds are readily synthesized by addition of amine to the ether solution of the sulfinic acid. Most of the salts are stable in air. Salts of secondary and tertiary aromatic amines, such as the methylaniline or dimethyl-*p*-toluidine salts, are very efficient accelerators in the benzoyl peroxide-initiated polymerization. However, colored products are formed. Aliphatic amine salts as well as the free acid give colorless polymers, but the setting time is increased considerably. Heterocyclic amines show reduced activity as polymerization accelerators. The setting times of monomer–polymer mixtures containing some of these accelerators have been determined. Physical properties of the polymers have been evaluated by measuring their resistance to indentation and recovery.

Résum

On a étudié l'efficacité des sels d'amines d'acides para-toluène-sulfiniques comme accélérateurs de polymérisation du méthacrylate de méthyle. Ces composés sont facilement synthétisés par addition de l'amine à la solution éthérée de l'acide sulfinique. La plupart des sels sont stables à l'air. Les sels d'amines aromatiques secondaires et tertiaires, telles la méthylaniline et la diméthylaniline, sont des accélérateurs très efficaces dans le cas des polymérisations initiées au peroxyde de benzoyle. Toutefois les produits finaux sont colorés. Les sels d'amines aliphatiques de même que les acides libres fournissent des polymères incolores; le temps nécessaire à la réaction est toutefois considérablement accru. Les amines hétérocycliques ne manifestent qu'une activité réduite comme accélérateur de polymérisation. Les temps de prise de mélanges monomère-polymère contenant certains de ces accélérateurs ont été déterminés. Les propriétés physiques des polymères ont été évalués en mesurant leur résistance à l'usage.

Zusammenfassung

Es wurde eine Untersuchung der Wirksamkeit von Aminsalzen von *p*-Toluolsulfinsäure als Beschleunigungsmittel in der Polymerisation von Methylmethacrylat ausgeführt. Diese Verbindungen werden leicht durch Zugabe von Amin zu einer ätherischen Lösung von Sulfinsäure synthetisiert. Die meisten Salze sind an der Luft beständig. Salze von sekundären und tertiären aromatischen Aminen, wie Methylanilin- oder Dimethyl-*p*-Toluidin-Salze, sind sehr wirksame Beschleunigungsmittel in der durch Benzoylperoxyd initiierten Polymerisation. Es werden jedoch farbige Produkte gebildet. Aliphatische Aminsalze wie auch die freie Säure ergeben farblose Polymere, aber die Erstarrungszeit ist erheblich höher. Heterocyclische Amine zeigen eine reduzierte Aktivität als Beschleunigungsmittel der Polymerisation. Die Erstarrungszeiten von Monomer–Polymer–Gemischen, die einige dieser Beschleunigungsmittel erhalten, wurden bestimmt. Physikalische Eigenschaften der Polymere wurden durch Messung ihres Widerstandes gegen Eindrücken und Widerherstellung evaluiert.

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