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Relative Inhibitory Effect of Various Compounds on the Rate of Polymerization of Methyl Methacrylate

K. K. GEORGIEFF, *Research Laboratories, Shawinigan Chemicals Limited, Shawinigan Falls, Quebec, Canada*

Synopsis

The relative inhibitory effect of the following compounds on the bulk polymerization of methyl methacrylate were measured: hydroquinone, *p-tert*-butylcatechol, *p*-methoxyphenol, 2,4-dichloro-6-nitrophenol, *n*-propyl gallate, di-*tert*-butyl-*p*-cresol, 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol), 1-amino-7-naphthol, *p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, 2-amino-1,4-naphthoquinone, three aminoanthraquinones, diphenylamine, *p*-nitrosodimethylaniline, α- and β-naphthylamine, phenothiazine, *N*-nitrosodimethylamine, hexamethylphosphoramide, *n*-dodecyl mercaptan, benzenethiol, 2,2-diphenyl-1-picrylhydrazyl, phenyl hydrazine, divinylacetylene, and various antimony and copper salts. Polymerization was carried out in a test tube in a bath at 101.2°C., benzoyl peroxide being used as initiator. Generally, phenols and naphthols were the strongest inhibitors, followed by quinones, aromatic amines, 2,2-diphenyl-1-picrylhydrazyl, antimony pentachloride, phenyl hydrazine, divinylacetylene, and the thiols.

The inhibitory effect of various phenols,[1–5] quinones,[4,6–11] amines,[2,7,12–17] thiols,[18,19] 2,2-diphenyl-1-picrylhydrazyl,[7] metallic salts,[20–22] and other compounds[23] on the rate of polymerization of methyl methacrylate have been studied. However, these results are difficult to compare due to differing experimental conditions. Hence, an exploratory investigation was carried out to establish which are the most effective and economical inhibitors (stabilizers) for industrial use.

A polymerization activity test was developed recently for the rapid evaluation of inhibitors.[24] In it, a 10-ml. portion of methyl methacrylate is heated with 0.0400 g. of benzoyl peroxide in a test tube immersed in a bath at 101.2°C. and the time required to reach a spontaneous boil measured. Since the temperature used is close to the atmospheric boiling point of methyl methacrylate, the conditions of the test represent the most drastic ones that are likely to be encountered in industrial operations.

Experimental

Commercial methyl methacrylate was distilled under reduced pressure to remove any low boiling impurities, high boilers, and stabilizer. It was then stored in a freezer at −70°C. until a few minutes before using. Known concentrations of each of the inhibitors listed below were made up in methyl methacrylate and the mixtures polymerized in accordance with the pro-

cedure described previously.[24] Unstabilized monomer was similarly polymerized.

Most of the inhibitors were purchased and were used as received. In most cases no attempt was made to establish the purity. The compounds are listed below in the order in which they appear in Table I. Hydroquinone was purified grade from J. T. Baker Chemical Co. *p-tert*-Butylcatechol (Catalog No. P 4583, practical grade) and *p*-methoxyphenol (Catalog No. 350) were obtained from Eastman Kodak Co. 2,4-Dichloro-6-nitrophenol was prepared by reacting a mixture of one part of 2,4-dichlorophenol and two parts of water with 260% of the theoretical amount of 70% nitric acid at 45–98°C. After recrystallization from benzene, its melting point was 124–125°C. *n*-Propyl gallate was reagent grade from British Drug Houses Ltd. Di-*tert*-butyl-*p*-cresol (Oxygard) was from Naugatuck Chemicals, while 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (Antioxidant No. 2246) was from American Cyanamid Co. 1-Amino-7-naphthol was technical grade from E. I. du Pont de Nemours Co. *p*-Benzoquinone was purified grade from Fisher Scientific Co. (Catalog No. Q-36). 2,6-Dichloro-*p*-benzoquinone (Catalog No. 3835), 2-amino-1,4-naphthoquinone (Catalog No. 5665), and 1-aminoanthraquinone (Catalog No. P 1387, practical grade) were obtained from Eastman Kodak Co. 1,4-Diaminoanthraquinone was technical grade from E. I. du Pont de Nemours. 1-Amino-4-hydroxyanthraquinone was practical grade from Eastman Kodak (Catalog No. P 6248). Diphenylamine was certified, A.C.S. grade from Fisher Scientific Co. (Catalog No. D-97). *p*-Nitrosodimethylaniline was from K & K Laboratories Inc. α-Naphthylamine was from Eastman Kodak Co. (Catalog No. 172); β-naphthylamine was of unknown origin. Phenothiazine was N.F. grade from Fisher Scientific

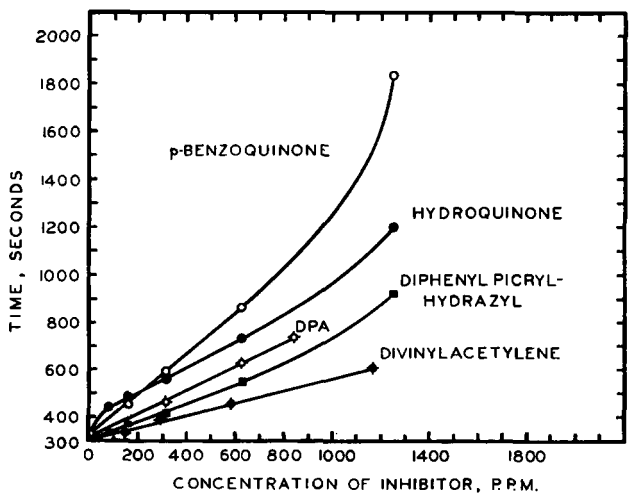

Fig. 1. Time lapse until spontaneous boiling of methyl methacrylate vs. concentration of various inhibitors added.

Co. (Catalog No. P-81.) *N*-Nitrosodimethylamine was from Eastman Kodak Co. (Catalog No. 7370). Hexamethylphosphoramide was from Monsanto Chemical Co. n-Dodecyl mercaptan was from Hooker Electrochemical Co., while benzenethiol was from Eastman Kodak Co. (Catalog No. 247). The stable free radical, 2,2-diphenyl-1-picrylhydrazyl was prepared by oxidizing 2,2-diphenyl-1-picrylhydrazine (Eastman Kodak, Catalog No. 7365) with lead dioxide and recrystallizing first from chloroform and then from a mixture of chloroform and ether.[25] It assayed a little more than 100% by titration with methanolic hydroquinone. Phenyl hydrazine was certified reagent grade (at least 99% pure) from Fisher Scientific Co. (Catalog No. P-86). Divinylacetylene was prepared by passing acetylene through an aqueous solution of cuprous chloride, ammonium chloride, and hydrochloric acid at 80°C. and distilling the crude product in a Podbielniak column under reduced pressure.[26] Antimony pentachloride was reagent grade (assay 100%) from J. T. Baker Chemical Co. Antimony trichloride was analytical reagent grade from Mallinckrodt Chemical Works. Copper resinate was technical grade.

Results

The time required for the sample to reach a spontaneous boil, in seconds, was plotted against the concentration of each inhibitor, and the inhibition factor calculated. (The inhibition factor is defined as the number of seconds by which the spontaneous boil is delayed per part per million of inhibitor.) In the case of the strongly inhibiting phenols, the initial part of the plot was found to be a curve and hence inhibition factors had to be calculated for various concentrations of inhibitor (cf. Table I and Fig. 1). The middle portion of the plot was a straight line and the final part a rapidly ascending curve representing the region in which the concentration of inhibitor was almost sufficient to prevent polymerization. For the other inhibitors studied, the initial portion of the plot appeared to be a straight line within the limits of experimental error, as was found previously for various unsaturated aliphatic inhibitors of vinyl acetate.[29,30] Thus, the retardation of the spontaneous boil of methyl methacrylate is proportional to the first power of the original inhibitor concentration except in the case of the strongly inhibiting phenols. With the latter, the power of the original concentration is somewhat greater than one.

From Table I, it will be noted that of the several classes of compounds studied, the phenols and naphthols were the strongest inhibitors. The dihydroxybenzenes, e.g., hydroquinone and *p-tert*-butylcatechol, were found to be substantially stronger than the monohydroxy compounds, e.g., *p*-methoxyphenol. The difference between hydroquinone and *p*-methoxyphenol was somewhat greater than that found by Caldwell and Ihrig[5] at 44.4°C. with 2,2′-azobisisobutyronitrile as initiator. From the work of these same authors,[5] the trihydroxybenzenes, for the most part, appear to be slightly stronger than the dihydroxybenzenes. The addition of the electron-withdrawing *p*-nitro group to phenol was found previously to

TABLE I
Inhibition Factors of Various Inhibitors[a]

Inhibitor	Inhibition factors, sec./ppm, at various concentrations								
	78.1 ppm	156.2 ppm	312.5 ppm	625 ppm	1250 ppm	2500 ppm	5000 ppm	10,000 ppm	27,000 ppm
Hydroquinone	1,40	1.01	0.74	0.65	0.70	[b]			
p-tert-Butylcatechol		0.75	0.57	0.47	0.42				
p-Methoxyphenol		0.58	0.37	0.28	0.25	0.23			
2,4-Dichloro-6-nitrophenol						0.051	0.068		
n-Propyl gallate					0.13		0.071		
Di-*tert*-butyl-*p*-cresol					0.0077	0.0071			
2,2'-Methylenebis-(4-methyl-6-*tert*-butylphenol)					0.13		0.072		
1-Amino-7-naphthol		0.63	0.45	0.51	[c]	[b]			
p-Benzoquinone		0.83	0.83	0.86	1.20	[b]			
2,6-Dichloro-*p*-benzoquinone			1.00	1.00	1.14	[b]			
2-Amino-1,4-naphthoquinone				0.11	0.11	0.11			
1-Aminoanthraquinone						0.03			
1,4-Diaminoanthraquinone									
1-Amino-4-hydroxyanthraquinone			0.084	0.088	0.133	0.18			
Diphenylamine			0.50	0.50	0.50[e]				
p-Nitrosodimethylaniline		0.55	0.57	0.64	[b]				
α-Naphthylamine		0.46	0.46	0.57	[c]	[b]			
β-Naphthylamine			0.42	0.53	[b]	[b]			
Phenothiazine			0.22[f]	0.23[f]		[b]			

N-Nitrosodimethylamine						0.008			
Hexamethylphosphoramide								0.003	
n-Dodecyl mercaptan					0.038	0.038	0.029		
Benzenethiol				0.105	0.110	0.083	0.102	[c]	
$Na_2S \cdot 9H_2O$	[d]								
2,2-Diphenyl-1-picrylhydrazyl			0.39	0.39	0.49				
Phenyl hydrazine			0.31	0.31	0.26	[b]			
Divinylacetylene		0.26	0.26	0.26	0.26				
Antimony pentachloride			0.36	0.28	0.19	0.12	0.07		
Antimony trichloride								0.004	
Copper resinate									0.005[f]
$CuSO_4$	[d]								
$Cu(OAc)_2$	[d]								
Methylene blue	[d]								
L-Ascorbic acid	[d]								
Cyanuric acid	[d]								

[a] Uninhibited methyl methacrylate required 300–320 sec. to reach a spontaneous boil.
[b] Showed no indication of polymerization after 40 min.
[c] Polymerized slowly without reaching a boil.
[d] Very low.
[e] Maximum concentration studied = 850 ppm
[f] Results erratic.

reduce very greatly its reactivity index.[5] Hence, the very low inhibition factor obtained in this investigation for 2,4-dichloro-6-nitrophenol (cf. Table I) in comparison to those of *p*-methoxyphenol, etc., is probably due, in part at least, to the presence of this group. The addition of a carboxylic group to the phenolic nucleus, e.g., *n*-propyl gallate, also appeared to reduce the inhibition factor to a very low level, since it has already been shown that unsubstituted 1,2,3-trihydroxybenzene is approximately as strong an inhibitor as hydroquinone.[5] Highly substituted, sterically hindered phenols such as di-*tert*-butyl-*p*-cresol and 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol), which are widely used in industry as antioxidants, were found to be weak inhibitors.

Only one naphthol, i.e., 1-amino-7-naphthol, was studied. It was found to be slightly stronger than the monohydroxybenzene, *p*-methoxyphenol, which is a widely used inhibitor for vinyl monomers. Thus by analogy, some of the naphthalene diols should be slightly stronger inhibitors than the benzene diols. This already has been shown to be true by previous investigators.[5] Therefore, the benzene diols and triols, and the naphthalene diols appear to be the most effective inhibitors which have been studied, and they are probably the most economical ones available commercially.

There are, of course, great differences in the inhibition factors of the various isomers of the benzene diols and triols, and the naphthalene diols. In the case of the benzene diols, little difference was found between the *para* and the *ortho* isomers (on a molar basis), thus confirming the results of previous investigators, but the *meta* form has been found to be much weaker.[5] With the benzene triols, the 1,2,4 isomer appears to be slightly stronger than the 1,2,3, and the latter is very much stronger than the 1,3,5.[5] Of the naphthalene diols, the 1,6 and the 1,5 forms appear to be strong inhibitors, while the 1,4 is weak.[5]

The quinones were the second strongest class of inhibitor. The *p*-benzoquinones were much stronger than the 1,4-naphthoquinones, which in turn were considerably stronger than the anthraquinones. The addition of two chlorine atoms to *p*-benzoquinone at the 2,6-positions enhanced the inhibition factor somewhat but the increase was much less than that which might have been expected from the results of Kice at 44.1°C. with 2,2′-azobisisobutyronitrile as initiator.[9] Kice also reported that when the number of chlorine atoms was further increased to four (i.e., chloranil), the terminator rate constant decreased to 5% of that of benzoquinone. Addition of amino groups to naphthoquinone and anthraquinone did not enhance their inhibitory effect substantially, but the addition of a hydroxyl group to anthraquinone did. The inhibition factor of *p*-benzoquinone was found to be a little lower than that for hydroquinone at the lower concentrations and somewhat higher at the higher concentrations. Caldwell and Ihrig[6] found that the fractional degree of retardation (relative to the unretarded rate for the same initiator concentration) for *p*-benzoquinone was 0–5% lower than for hydroquinone at 44.4°C. When allowance is made for differences in the experimental conditions used in these two investigations, agreement in results can be considered quite good.

Aromatic amines were the next strongest class of inhibitor, being 50–75% as strong as hydroquinone at the lower concentrations. The difference between the mono- and diphenylamines was relatively small, as was the difference between the phenylamines and the naphthylamines, e.g., diphenylamine and α-naphthylamine respectively. α-Naphthylamine was found to be slightly stronger at the lower concentrations than the β-naphthylamine, but a rigorous comparison is not justified since the purities of the two compounds was not very high. Foord[27] found the β-compound a stronger inhibitor than the α-naphthylamine in the polymerization of styrene. Cyclic aromatic amines, e.g., phenothiazine, were much weaker than the noncyclic amines. Aliphatic amines and amides, e.g., *N*-nitrosodimethylamine and hexamethylphosphoramide, respectively, were almost without inhibitory effect.

Both organic and inorganic sulfur compounds were studied, but all proved to be very weak inhibitors (chain transfer agents). Aromatic thiols were stronger chain transfer agents than the aliphatic. For example the inhibition factor for benzenethiol was found to be 2.2–3.5 times as great as that of *n*-dodecyl mercaptan. This is in good agreement with the results of O'Brien and Gornick,[18] who found that the chain transfer constant C_s at 60°C. for benzenethiol was four times that of 1-butanethiol, a compound which should have the same order of activity as dodecyl mercaptan. Sodium sulfide was found to have almost no inhibitory effect, probably due to its low solubility in methyl methacrylate.

The stable free radical, 2,2-diphenyl-1-picrylhydrazyl, was found to have an inhibition factor about half that of hydroquinone and *p*-benzoquinone on a weight basis or about twice as great on a molar basis. Kice[7] determined the value of k_x/k_p for the hydrazyl and concluded that at 44.1°C. the free radical was 400 times more reactive toward methyl methacrylate radical than benzoquinone during the induction period. After the induction period the rate of polymerization was unretarded. Some of the reasons for the apparent magnitude of the difference in these results can be readily explained. Our measurements were a sum of the induction period and the time required to polymerize a large percentage of the monomer, while those of Kice involved only the induction period. During the polymerization the purple color of the hydrazyl slowly faded and finally disappeared. Bartlett and Kwart[28] observed this same phenomenon with vinyl acetate and concluded that the disappearance of the purple color indicated the end of the induction period. The same conclusion is undoubtedly true in the case of methyl methacrylate. Hence, during a large percentage of the time in our polymerizations, a secondary species derived from the hydrazyl free radical was the true inhibitor. The apparent inhibition factor for the hydrazyl was only moderately greater than that for phenyl hydrazine, a compound closely related to 2,2-diphenyl-1-picrylhydrazine, which is the reduced form of the hydrazyl. This suggests that the secondary species of inhibitor may be a hydrazine. A much less important reason for the apparent discrepancy with Kice's results was the great difference in polymerization temperature, i.e., about 60°C. While only one temperature

(101°C.) was studied in the present investigation with methyl methacrylate, a lower temperature (70°C.) was studied with vinyl acetate by using the test tube procedure described previously.[29] The apparent inhibition factor for 2,2-diphenyl-1-picrylhydrazyl in vinyl acetate was found to be about 16% greater than that for hydroquinone. While this suggests that the free radical is relatively more effective at lower temperatures, probably due to greater stability, the discrepancy due to the difference in polymerization temperatures can only be a small fraction of the total. In the case of vinyl acetate at 70°C., the purple hydrazyl color disappeared within a few minutes, thus indicating that most of the inhibition measured was due to a secondary species of the hydrazyl. In any case, it is apparent that the free radical has little practical value as an inhibitor at temperatures approaching 100°C. It may have some value at lower temperatures, but its inherent instability mitigates against this too.

Only one polyenyne inhibitor, i.e., divinylacetylene (DVA), was studied. This compound was previously found to be a very strong inhibitor in the polymerization of vinyl acetate and acrylonitrile.[29,31] In the polymerization of vinyl acetate, it was stronger than hydroquinone,[30] but in the case of methyl methacrylate, it was found to be only about one-fifth as strong. This may have been due in part to loss of DVA during the test, since the bath temperature was kept about 16°C. higher than the atmospheric boiling point of this compound. When the time required to reach a spontaneous boil was plotted against each concentration of DVA in methyl methacrylate, a straight line was obtained, at least up to a concentration of 1160 ppm. A similar linear relationship was found previously with DVA in vinyl acetate.[29]

The salts of only two metals were studied, i.e., antimony[20] and copper.[21,22] Of these, antimony pentachloride was found to have the highest inhibition factor, being about half that of hydroquinone at the lower concentrations. Antimony trichloride, on the other hand, was almost without inhibitory effect. Of the copper salts, only the resinate exhibited a very weak inhibition. The acetate and sulfate were without any effect, probably due to their insolubility in methyl methacrylate.

Three other compounds which have found use as inhibitors for other vinyl monomers, i.e., methylene blue, L-ascorbic acid,[23] and cyanuric acid, exhibited no inhibitory effect, possibly due to their insolubility.

Inhibition by Mixtures of Inhibitors

With 1:1 mixtures (by weight) of hydroquinone–*p*-*tert*-butylcatechol and hydroquinone–*p*-methoxyphenol, no synergistic effect was obtained (cf. Table II). In fact, the experimentally derived inhibition factors were slightly lower than the ones calculated from the individual inhibition factors at the same concentration as present in the mixture. With a mixture of hydroquinone and *p*-benzoquinone, a significant synergesis was obtained at concentrations of about 900–2500 ppm of mixture. With the mixtures hydroquinone–diphenylamine, quinone–diphenylamine, and *p*-*tert*-butylcatechol–phenothiazine, the synergesis was considerably greater

TABLE II
Inhibition Factors of 1:1 Mixtures of Inhibitors

Inhibitor mixture	Total conc. of inhibitors, ppm	Inhibition factors, sec./ppm	
		Experimental	Calculated
Hydroquinone and *p-tert*-butylcatechol	312.5	0.74	0.88
	625	0.63	0.66
	1250	0.55	0.56
Hydroquinone and *p*-benzoquinone	312.5	0.87	0.92
	625	0.80	0.79
	1250	0.96	0.76
	2500	>2.3	0.95
Hydroquinone and diphenylamine	625	0.61	0.62
	960	0.69	0.59
	1300	1.15	0.58
	2500	>400	
p-Benzoquinone and diphenylamine	312.5	0.85	0.67
	625	0.73	0.67
	940	0.91	0.68
	1250	1.35	0.68
	2500	>515	
p-tert-Butylcatechol and phenothiazine	1250	0.8	0.35

in the same general range of concentration. It thus appears that the two components of the mixture must be of a different chemical class in order to obtain a fairly large synergistic effect. It also appears that as the chemical constitutions of the components become more similar the synergesis decreases. However, it will be necessary to study a much larger number of mixture combinations before one can establish whether the above generalizations have wide applicability.

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Résumé

On a mesuré l'effet inhibiteur relatif des composés suivants sur la polymérisation en bloc du méthacrylate de méthyle: hydroquinone, *p-tert*-butylcatéchol, *p*-méthoxyphénol, 2,4-dichloro-6-nitrophénol, gallate de *n* propyle, di-*tert*-butyl-*p*-crésol, 2,2'-méthylène-bis(4-méthyl-6-*tert*-butylphénol), 1-amino-7-naphtol, *p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, 2-amino-1,4-naphtoquinone, trois aminoanthraquinones, diphénylamine, *p*-nitrosodiméthylaniline, α- et β-naphtylamines, phénothiazine, *N*-nitrosodiméthylamine, hexaméthylphosphoramide, *n*-dodécyl mercaptan, benzènethiol, 2,2-diphényl-1-picrylhydrazyl, phénylhydrazine, divinylacétylène, et différents sels d'antimoine et de cuivre. La polymérisation a été effectuée dans un tube à 101.2°C avec du peroxyde de benzoyle comme initiateur. Généralement, les phénols et les naphtols sont les inhibiteurs les plus puissants suivis par les quinones, les amines aromatiques, le 2,2-diphényl-1-picrylhydrazyl, le pentachlorure d'antimoine, la phénylhydrazine, le divinylacétylène et les thiols.

Zusammenfassung

Die relative Inhibitorwirkung folgender Verbindungen auf die Polymerisation von Methylmethacrylat in Substanz wurde gemessen: Hydrochinon, *p-tert*-Butyl-brenzcatechin, *p*-Methoxyphenol, 2,4-Dichlor-6-nitrophenol, *n*-Propylgallat, Di-*tert*-Butyl-*p*-cresol, 2,2'-Methylen-bis-(4-methyl-6-*tert*-butylphenol), 1-Amino-7-naphthol, *p*-Benzochinon, 2,6-Dichlor-*p*-benzochinon, 2-Amino-1,4-naphthochinon, drei Aminoanthrachinone, Diphenylamin, *p*-Nitrosodimethylanilin, α- und β-Naphthylamin, Phenothiazin, *N*-Nitrosodimethylamin, Hexamethylphosphoramid, *n*-Dodecylmercaptan, Phenylmercaptan, 2,2-Diphenyl-1-picrylhydrazyl, Phenylhydrazin, Divinylacetylen und verschiedene Antimon- und Kupfersalze. Die Polymerisation wurde in einer Proberöhre in einem Bad bei 101,2°C mit Benzoylperoxyd als Starter ausgeführt. Im allgemeinen waren Phenole und Naphthole die stärksten Inhibitoren, gefolgt von Chinonen, aromatischen Aminen, 2,2-Diphenyl-1-picrylhydrazyl, Antimonpentachlorid, Phenylhydrazin, Divinylacetylen und den Thiolen.

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