

Methyl Methacrylate Stabilization by Sodium Borohydride

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Synopsis

Sodium borohydride was examined as a polymerization inhibitor for methyl methacrylate and found to be more effective than hydroquinone-type inhibitors in preventing polymerization during monomer storage under nitrogen at elevated temperature. NaBH_4 appears to function by reducing peroxide and hydroperoxide impurities that form during monomer storage. Unlike conventional free radical inhibitors, NaBH_4 does not interfere with azo initiator systems. In peroxide-initiated systems, the inhibitory effect of NaBH_4 can be overcome by simple acidification.

INTRODUCTION

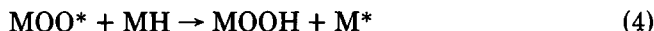
Many monomers require stabilization with free-radical inhibitors to prevent spontaneous polymerization during storage. The initiation step responsible for this polymerization is not clearly understood but probably involves the action of heat or light on certain impurities or functional groups present in the monomer, such as carbonyl groups or carbon-carbon double bonds, to form free radical species which combine with unactivated monomer to initiate polymerization:



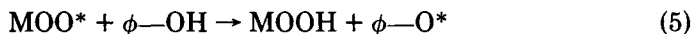
In the presence of oxygen, however, M^* preferentially reacts with oxygen to form peroxy radicals:



The peroxy radical can then abstract a labile hydrogen from additional monomer, forming a hydroperoxide and another monomer radical:



Phenolic inhibitors compete with the reaction as shown in eq. (4), thereby preventing formation of additional monomer radicals:



As long as oxygen is present, it will react with any M^* to form peroxy radicals and the phenol will prevent the peroxy radicals from producing more M^* . Hence, the phenol and O_2 work together to stabilize the monomer.

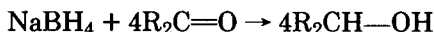
A problem arises, however, as the hydroperoxide level builds up. The hydroperoxide is capable of breaking down into radical species, eq. (6), which in turn may abstract hydrogen, activating more monomer, eq. (7):





Eventually the hydroperoxide concentration may become so high that there is not enough O_2 present to trap all the M^* . Another possibility is that the O_2 present in the atmosphere above the monomer may be consumed by the surface monomer only, allowing polymerization to occur in the lower portions where the oxygen supply has been exhausted by the high hydroperoxide concentration. In either case, when M^* cannot react with O_2 , it will react according to eq. (2), resulting in premature polymerization. It is therefore desirable to reduce the hydroperoxides to stable nonradical products.

We have examined the possibility of using sodium borohydride to control the buildup of hydroperoxide during monomer storage.^{4,5} Sodium borohydride is widely used on an industrial scale to reduce trace carbonyl and peroxide impurities in a variety of organic chemicals (alcohols, glycols, esters, ethers):



EXPERIMENTAL

Because of the well-known tendency of methyl methacrylate (MMA) to form hydroperoxides during storage,^{1,2} this monomer was selected as suitable for testing the efficacy of NaBH_4 as a monomer stabilizer.

MMA containing 65 ppm hydroquinone monomethyl ether (MEHQ) (Aldrich) or 50 ppm MEHQ (Mallinckrodt) was treated to remove the inhibitor by three extractions with twice its volume of a solution of 0.5% (w/w) NaOH and 5% (w/w) Na_2SO_4 , followed by water washes and drying over magnesium sulfate.

Monomer stability studies were conducted by subjecting MMA samples (as received, inhibitor free, or inhibited with NaBH_4) to elevated temperature storage in thick-walled clear glass bottles suspended in a controlled-temperature oil bath. Both inert (N_2) and air atmospheres were evaluated. Monomer stability was evaluated by removal of aliquots during heating and adding these aliquots to methanol to detect trace quantities of polymer precipitate.

The solubility of NaBH_4 in MMA was determined using the recently reported crystal violet titration method⁶ and was found to be 58 ppm as NaBH_4 at 25°C.

As an alternative to NaBH_4 , the more soluble tetrabutylammonium borohydride was evaluated. Bu_4NBH_4 was made by extracting aqueous solutions of tetrabutylammonium hydrogen sulfate (Aldrich) and sodium borohydride (Alfa) with methylene chloride.⁷ The dry product was obtained by stripping off the methylene chloride under vacuum.

RESULTS

Storage Stability

Table I summarizes the results of experiments in which methyl methacrylate, with and without inhibitors, was heated for prolonged periods of time. The onset of polymerization was taken to be the time when aliquots pipetted into methanol gave a white precipitate. In samples left open to air during heating, sodium

TABLE I
Elevated Temperature Stability of Methyl Methacrylate

• Inhibitor	Treatment conditions	Hours to onset of polymerization ^a
None		4.5
107 ppm NaBH ₄	80–90°C, open to air	11.5
65 ppm MEHQ		>11.5
None		5
107 ppm NaBH ₄	85–95°C, open to air	10
214 ppm NaBH ₄		13
50 ppm MEHQ		>13
None		14
125 ppm NaBH ₄		>116 ^c
250 ppm NaBH ₄	80–95°C, N ₂	>116 ^c
110 ppm Bu ₄ NBH ₄ ^b		72–87 ^d
50 ppm MEHQ		70

^a Determined by aliquot addition to methanol.

^b Tetrabutylammonium borohydride; made in house.

^c Samples gave no precipitate in methanol even after 116 hr.

^d Sample polymerized somewhere between 72 and 87 hr.

borohydride increased the time required for onset of polymerization by a factor of 2 to 3 as compared with the uninhibited sample. However, sodium borohydride was less effective than MEHQ in stabilizing monomer exposed to air during elevated temperature storage (80–95°C).

Sodium borohydride is more effective than MEHQ as a stabilizer when the MMA is sealed under N₂ during elevated temperature storage (90 ± 5°C). (See the third set of examples in Table I.) The uninhibited sample showed polymer formation after 14 hr. Polymer formation was observed after 70 hr in the sample containing MEHQ, whereas the NaBH₄-treated samples showed no polymer formation after 116 hr.

MMA treated with NaBH₄ did develop a small amount of flocculent white precipitate within an hour after heating was begun. But since aliquot addition to methanol gave no white precipitate, the material in the monomer did not appear to be poly(methyl methacrylate) (PMMA). Isolation by filtration and analysis of the flocculent white precipitate (IR, emission spectrum, and x-ray diffraction) indicated that the material was not polymeric but was a borate (16% boron). Use of tetrabutylammonium borohydride stabilized the MMA up to 72 hr and did not cause the formation of an insoluble white precipitate.

Mode of Action

To establish that NaBH₄ stabilizes MMA by reducing peroxides rather than scavenging radicals, azo and peroxide initiators were added to NaBH₄-stabilized monomer prior to heating. The results are summarized in Table II. Trials 1 through 7 indicate that NaBH₄ had no effect in inhibiting polymerization in the presence of an azo initiator, azobisisobutyronitrile (AIBN). If hydride anion H⁻ were acting as a radical trap, complete inhibition of polymerization would be expected in trials 1 through 5 where H⁻ is in excess. In trials 6 and 7, in which

TABLE II
 Treatments Carried Out in Presence of Azo or Peroxide Initiators

Trial no.	Treatment level	R* to H ⁻ ratio	Conditions ^a	Results
1	0.4% AIBN + 1000 ppm NaBH ₄	1:2	70°C/N ₂ /10 min	aliquots removed after 10 min; all three precipitated polymer in MeOH
2	0.4% AIBN + 65 ppm MEHQ		70°C/N ₂ /10 min	
3	0.4% AIBN		70°C/N ₂ /10 min	
4	0.05% AIBN + 120 ppm NaBH ₄	1:2	76 ± 2°C/N ₂ /1 hr	both samples increased in viscosity until solid at end of 1 hr
5	0.05% AIBN		76 ± 2°C/N ₂ /1 hr	
6	0.5% AIBN + 100 ppm NaBH ₄	6:1	70–90°C/air/15 min	both samples violently polymerized 5 min after removal from heat
7	0.5% AIBN		70–90°C/air/15 min	
8	0.5% B.P. ^b + 120 ppm NaBH ₄	3:1	70–90°C/N ₂ /15 min	20 min induction period after heating
9	0.5% B.P. + 65 ppm MEHQ		70–90°C/N ₂ /15 min	no induction period after heating
10	0.5% B.P.		70–90°C/N ₂ /15 min	no induction period after heating
11	0.5% C.H. ^c + 150 ppm NaBH ₄	4:1	92 ± 1°C/N ₂	2-hr induction period before polymerization
12	0.5% C.H. + 1200 ppm NaBH ₄	1:2	90 ± 1°C/N ₂	still fluid after 3.5 hr
13	0.5% C.H.		92 ± 1°C/N ₂	continual increase in viscosity; solid after 1.5 hr
14	0.5% C.H. + 1200 ppm NaBH ₄ + HCl ^d	1:2	92 ± 1°C/N ₂	continual increase in viscosity; solid after 1.5 hr

^a Samples removed from heat after time indicated.

^b Benzoyl peroxide.

^c Cumene hydroperoxide.

^d 1N HCl added after NaBH₄ but before cumene hydroperoxide.

AIBN radicals are in excess, an induction period would be expected, corresponding to the time required for all the H⁻ to be consumed. Neither result was observed. Polymerization by AIBN occurred equally well in stabilized (MEHQ or NaBH₄) and unstabilized samples.

Sodium borohydride did give results indicative of its function as a peroxide reducer in trials 8 through 14. In trials 8 through 10, where excess benzoyl peroxide was used, the presence of NaBH₄ resulted in a 20-min induction period, followed by a sudden and rapid increase in viscosity. Once all the borohydride

was consumed in reducing the peroxide, the remaining peroxide initiated polymerization. The uninhibited MMA and MEHQ-inhibited MMA both polymerized immediately after removal from the oil bath (trials 9 and 10).

In polymerizations initiated with cumene hydroperoxide, two NaBH_4 treatment levels were used, one in which hydride was in excess of hydroperoxide and one in which cumene hydroperoxide was in excess of hydride. An induction period occurred when cumene hydroperoxide was in excess (trial 11). Polymerization did not occur when hydride was in excess (trial 12).

In trial 14, 1N HCl was added to the MMA after addition of NaBH_4 but before addition of initiator. The HCl decomposed the NaBH_4 as evidenced by generation of a large quantity of gas (H_2). The sample then behaved as if NaBH_4 had never been added, that is, it polymerized in identical fashion as the control (trial 13).

DISCUSSION

Sodium borohydride is an effective stabilizer in methyl methacrylate during elevated temperature storage. Work done using peroxide initiator systems supports the conclusion that NaBH_4 functions by reducing peroxides and hydroperoxides which can lead to premature polymerization during storage.

The insoluble borate formed during elevated temperature storage of MMA stabilized with NaBH_4 can be removed simply by filtration. Alternatively, tetrabutylammonium borohydride may be used, which does not cause formation of a white precipitate.

The stabilizing action of NaBH_4 can be overcome by acidifying the MMA with HCl or other suitable acid. In systems which cannot tolerate addition of acid, stabilization can be overcome by using excess peroxide initiator.

Since NaBH_4 does not react with azo compounds, polymerizations utilizing azo initiators can be conducted without prior removal or inactivation of the NaBH_4 stabilizer.

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