

NATIONAL BUREAU OF STANDARDS REPORT

10 456

Progress Report
on
**A STABILIZING COMONOMER
PART II STABILIZATION AND
POLYMERIZATION CHARACTERISTICS**



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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A STABILIZING COMONOMER: PART II STABILIZATION AND POLYMERIZATION CHARACTERISTICS

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A STABILIZING COMONOMER: II. STABILIZATION
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Synopsis

The hardening times of an experimental composite material and the gel times of a two-liquid monomer formulation increased with higher concentrations of a stabilizing comonomer. The compound (BHM) polymerized under anaerobic conditions when initiated with 2-cyano-2-propyl radicals.

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The compound BHM (3,5-di-tert-butyl-4-hydroxybenzyl methacrylate) reported in Part I,¹ was evaluated with regard to its effectiveness as a stabilizer (polymerization inhibitor). The present paper describes these findings and verifies that the methacrylate portion of the molecule can polymerize.

Materials and Methods*

The polymerization-inhibiting capability of BHM was measured by two methods: (1) a "slide immobilization test"² of hardening time for a composite formulation and (2) a gel-time determination for an equal-volume mixture of two liquid formulations.

SLIDE IMMOBILIZATION TEST METHOD².—Liquid monomer formulations were prepared with Monomer X-980† (trimethylolpropane

* Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the material or equipment identified is necessarily the best available for the purpose.

† Rohm and Haas

trimethacrylate, as supplied with 200 ppm of the monomethyl ether of hydroquinone), 0.586% of N,N-dimethyl-3,5-xylidine, and various concentrations of BHM. Fifteen drops of liquid were mixed by hand spatulation with a powder containing 1.0% benzoyl peroxide dispersed on spheroidal particles of fused silica treated with 3-methacryloxypropyltrimethoxysilane, as described previously.² A homogeneous mix was prepared using as much powder as possible.

Each mixture was transferred immediately onto a clean, dry glass plate (3-1/4 x 4 inch). Spacers, (microscope slides, 1 mm thick) were placed around, but not touching, the mix, and another glass plate (with its long axis perpendicular to that of the bottom glass) was placed on the spacers, forcing the plastic material to form a disc about 20 mm in diameter. With the lower slide immobilized, the upper slide was gently moved a short distance (no greater than 1 mm) by hand, back and forth linearly every quarter minute. The time at which the upper slide could no longer be moved easily in this fashion was termed the "linear hardening time." Then a rotational force was

applied by twisting the upper slide about the approximate center of the specimen. The force was applied in a clockwise and then counterclockwise direction and the distance traversed was no more than about 3 degrees of an arc. The time at which the upper slide could no longer be perceptibly rotated relative to the lower slide, when considerable hand force was applied, was recorded as the "rotational hardening time."

GEL TIME DETERMINATION.—A stock solution was prepared with 47% methyl methacrylate* [as supplied with 35 ppm BHT (2,6-di-t-butyl-4-methylphenol)] and 53% "HEMA-phthalates"† (as supplied with somewhat less than 35 ppm BHT). The phthalate monomers have been described previously.^{3,4} The stock solution was divided into two parts. To one part was added sufficient N,N-dimethyl-3,5-xylidine to obtain a 1.03% solution of this amine accelerator. To the other part was added enough benzoyl peroxide‡ to give a 3.33% solution.

* Rohm and Haas

† The Epoxylite Corp.

‡ Lucidol[®]-98, Pennwalt Corp.

The solution containing the peroxide was further subdivided into portions into which were dissolved various amounts of BHM or BHT.

One cc of amine solution was injected, using a calibrated syringe with needle, into a small test tube supported beneath an automatic gel timer.* One cc from one of the peroxide solutions was injected forcefully into the same tube so as to mix the two solutions. The gel timer was immediately started; it automatically raised and lowered a disposable wooden cylindrical probe (2.2 to 2.3 mm in diameter) in the liquid mixture, further stirring the combined solutions. The probe had been adjusted to closely approach but not touch the bottom of the test tube. After the induction period, the length of which depended upon the inhibitor concentration and effectiveness, the gelling or solidifying immobilized the probe, automatically stopping the timer. The precision of this measurement was about 0.1 minute.

* "Tecam," Techne (Cambridge) Ltd., Duxford, England

POLYMERIZATION OF THE STABILIZING COMONOMER.—The colorless crystals of BHM (2.84 gm) were placed into a centrifuge tube provided with a rubber stopper and two valved ports. One port was connected to a low-pressure nitrogen source and the other was attached to a trap cooled in dry ice (solid carbon dioxide) and alcohol and thence to a vacuum pump. The container was evacuated and then refilled with nitrogen repeatedly. Meanwhile the crystals were melted in a steam bath. Since polymerization did not occur the first hour with the sample under vacuum at about 95-100°C, AIBN (α, α' -azo-bis-isobutyronitrile; 0.459%) was added and the pumping and heating processes were resumed. Within 30 minutes, the compound had polymerized to a hard, glassy, transparent and colorless solid. A portion of this was dissolved in deuterated chloroform for NMR analysis.

Results

SLIDE IMMOBILIZATION TEST.—The effectiveness of BHM in inhibiting polymerization is shown graphically in Figure 1. The plots, obtained by least-squares fitting of the data,^E appear to show a linear increase of hardening time with increase of BHM over the concentration range investigated.

GEL TIME.—The results given in Table 1 also demonstrate that BHM inhibits polymerization. The induction period increases with increasing concentration in a nearly linear manner. The efficiency is not as high as that of BHT, as the gel times are shorter for BHM at approximately equal molalities (concentrations in moles/kg of solvent).

The hardening times for BHT did not obey a linear relationship with concentration according to statistical tests.

The hardening times increased linearly (at the 95% confidence level) with the concentrations of BHM whether expressed in weight percentage or molality.⁶ When weighting factors (the reciprocals of the squares of the standard deviations of the hardening time data for each concentration)⁵ were used in linear least-square fitting, then the following relationships were obtained:

$$\text{the gel time} = 1.97 + 19.49 \underline{m},$$

$$\text{the linear hardening time} = 2.49 + 9.08 \underline{m} \text{ and}$$

$$\text{the rotational hardening time} = 3.13 + 13.56 \underline{m},$$

where \underline{m} is the concentration of BHM in moles per kg of solvent (monomers).

The linear relationship that exists between the rotational hardening times and the linear hardening times, was obtained from the data, assuming experimental error in both sets of measurements;⁷ thus the relationship was: rotational hardening time = 1.34 (linear hardening time) - 0.22, in minutes.

The monomer solution containing benzoyl peroxide and only about 30 ppm of BHT, the lowest concentration used, polymerized during storage at room temperature after only a few days, whereas none of the other solutions gelled during a much longer period.

HOMOPOLYMERIZATION.—The NMR spectrum of the polymerized compound (BHM) was consistent with homopolymer together with residual monomeric BHM. A segment of the polymer is shown in Figure 2.

Discussion

The effectiveness of BHM relative to BHT is in harmony with the mechanism that had been postulated for similar sterically-hindered phenols.⁸ The methyl group on the 4-position in BHT is more electron-releasing and less sterically hindering, compared to the corresponding methacryloxymethyl group of BHM. Since the efficiency of 3,6-di-t-butyl-4-substituted phenolic compounds is dependent upon the electron-releasing nature of, and lack of steric-hindrance by the 4-

substituent,⁸ a somewhat higher molar concentration of BHM (relative to BHT) would be required to obtain the same storage stability and working time for a given acrylic liquid or paste formulation.

The postulated mechanism of inhibition involves the removal of the phenolic hydrogen atom from the inhibitor by a molecule containing an oxygen atom with an unshared valence, or odd electron (free radical).^{8, 9} The molecule containing this oxygen atom might be a benzoyloxy initiator radical¹⁰ or a peroxy radical [formed by the facile addition of an atmospheric oxygen molecule (O_2) to a polymeric free radical during polymerization].¹¹ The inhibitor molecule then becomes a conjugated free radical that cannot appreciably initiate polymerization due to the delocalized nature of the odd electron (resonance stability)¹² but it can react with and terminate another free radical.

Due to the di-radical nature of molecular oxygen, which is present in any system from which it has not been specifi-

cally excluded, it reacts very readily with the carbon radicals in the growing polymer chains. The resulting peroxy radicals are relatively unreactive^{1,2} and thus slow to initiate polymerization of methacrylate monomers. Although peroxy^{4,5} and benzoyloxy radicals can react with phenolic inhibitors, these inhibitors are ineffective in the absence of air.^{1,2} Therefore, BHM could be polymerized in a vacuum when initiated with 2-cyano-2-propyl radicals derived from the thermal decomposition of AIBN.^{1,2}

Conclusions

A methacrylate monomer that contained a phenol-type polymerization inhibitor in the same molecule was evaluated. The times between mixing and hardening of methacrylate monomers containing small amounts of this compound increased linearly with the concentrations. The pure compound (BHM) could be polymerized by using an oxygen-free atmosphere, together with a free radical initiator (AIBN) that did not contain oxygen atoms.

Compounds such as this, which can stabilize monomers by inhibiting premature polymerization and can take part in the polymerization when the initiator system is activated, are worthy of further investigation.

The authors are grateful to Mr. R. A. Thompson of the National Bureau of Standards, for obtaining the NMR spectra.

TABLE 1

GEL TIMES FOR MONOMERS CONTAINING VARIOUS
CONCENTRATIONS OF BHT AND BHM STABILIZERS

<u>Stabilizer concentration</u>		<u>Gel time*</u>	<u>σ†</u>
%	molality‡	min.	min.
<u>BHT</u>			
0.003	0.0001	2.0	0.06
0.12	0.0105	2.5	0.16
0.66	0.0612	3.7	0.62
1.94	0.183	7.2	0.54
3.06	0.296	9.7	3.46
<u>BHM</u>			
0.22	0.0071	2.2	0.22
0.84	0.0279	2.7	0.22
4.16	0.143	4.7	0.36
5.95	0.208	5.8	0.77

* Average of 6 measurements made at room temperature

† Standard deviation: $\sqrt{\frac{\sum (x-\bar{x})^2}{n-1}}$

‡ Moles per kg of solvent

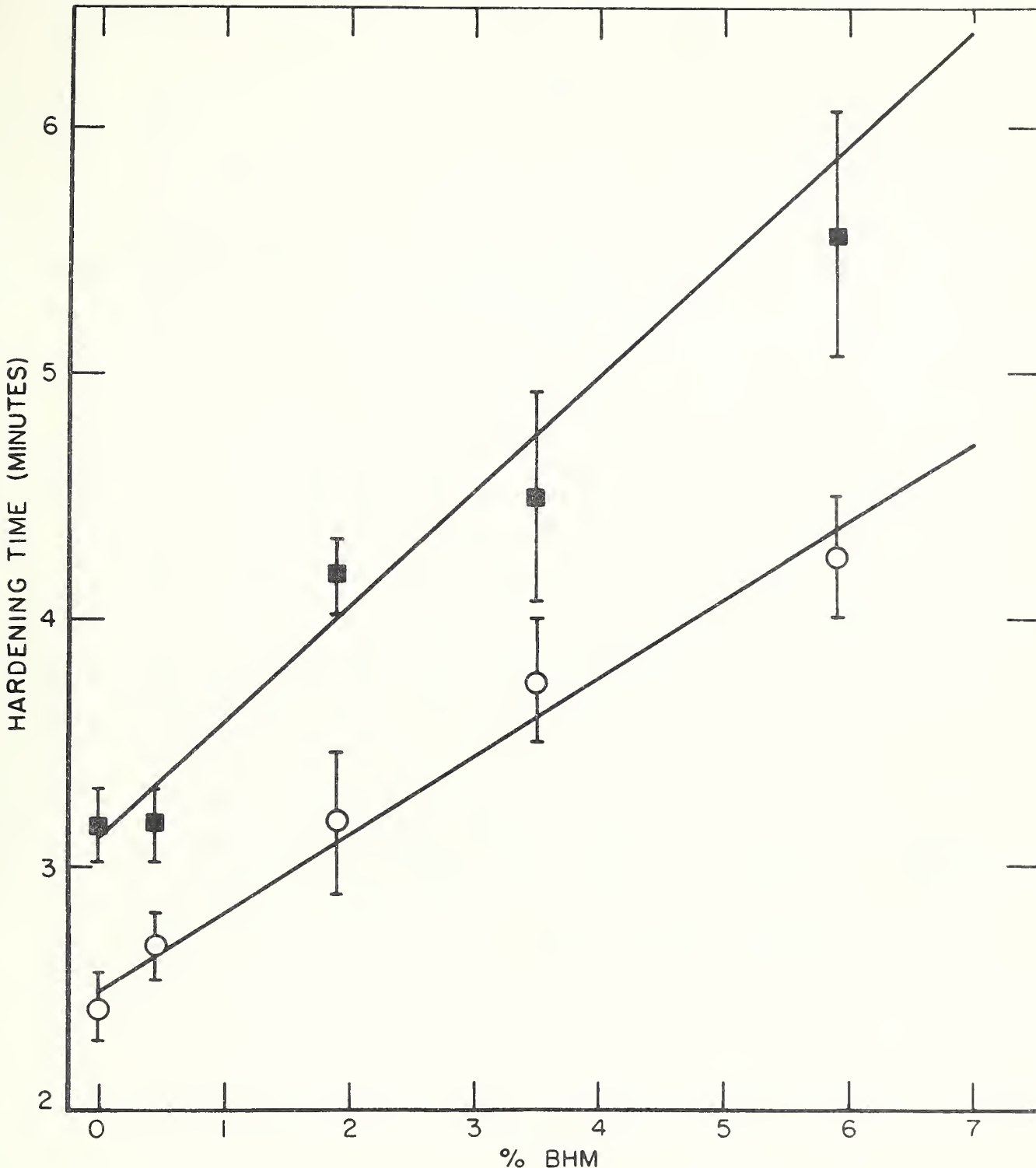


FIGURE 1:—Hardening times for a formulation of tri-methylolpropane trimethacrylate (as supplied with 0.02% of the monomethyl ether of hydroquinone) containing 0.586% N,N-dimethyl-3,5-xylylidine and varying concentrations of BHM. The average linear hardening times (○) and rotational hardening times (■), as defined in the text, increase with increasing BHM concentrations. The length of the vertical line from each symbol represents the standard deviation of three measurements. The lines were obtained by a least-square fitting of the data.

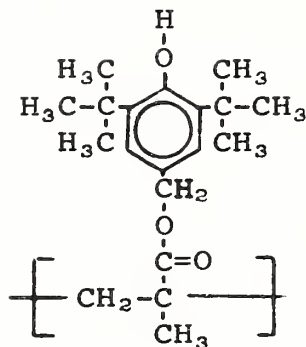


FIGURE 2.—Structural formula of a segment of polymerized or copolymerized BHM (3,5-di-tert-butyl-4-hydroxybenzyl methacrylate)

References

1. Bowen, R. L., and Argentar, H.: A Stabilizing Comonomer: I. Synthesis and Confirmation of Structure, (submitted to J Dent Res).
2. Bowen, R. L., and Argentar, H.: Amine Accelerators for Methacrylate Resin Systems (J Dent Res July-Aug 1971, in press).
3. Bowen, R. L.: Crystalline Dimethacrylate Monomers J Dent Res 49:810-815, 1970.
4. Bowen, R. L.: Ternary Eutectic Dimethacrylate Monomer System and Restorative Dental Material Prepared Therefrom, U. S. Patent 3,539,526, 1970.
5. Parratt, L. G.: Probability and Experimental Errors in Science, New York, John Wiley & Sons, Inc. 1961, pp 127-129.
6. Natrella, M. G.: Experimental Statistics NBS Handbook 91, Washington, D. C., U. S. Government Printing Office, 1963 6:7-21 and list of errata.
7. Mandel, J.: The Statistical Analysis of Experimental Data, New York, John Wiley & Sons, Inc. 1961, pp 288-292.
8. Ingold, K. U.: Inhibition of Oil Oxidation by 2,6-Di-t-butyl-4-substituted Phenols, J Phys Chem 64:1636-1642, 1960.
9. Lloyd, W. G., and Zimmerman, R. G.: Antioxidant Inhibition by Substituted Phenols, Ind and Eng Chem 4:180-185, 1965.

10. Kleiner, E. K. (to J. R. Geigy SA): Polymeric Antioxidants with Blocked Phenolic Groups, French Patent 2011412, 1970.
11. Georgieff, K. K.: Relative Inhibitory Effect of Various Compounds on the Rate of Polymerization of Methyl Methacrylate, J Appl Polymer Sci 9:2009-2018, 1965.
12. Walling, C.: Free Radicals in Solution, New York, John Wiley & Sons, Inc. 1957, pp 25, 70, 168-170.
13. Pryor, W. A.: Free Radicals, New York, McGraw-Hill Book Co. 1966, pp 290-295, 326.

