Polymerization Activity Test for Methyl Methacrylate

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Synopsis

Two activity (polymerization) tests have been developed for evaluating the purity of methyl methacrylate industrially. A 10-ml. portion of monomer is heated with 0.0400 g. of benzoyl peroxide in a test tube immersed in a bath at 101.2°C., until a spontaneous boil occurs. The effect of temperature, catalyst concentration, oxygen, barometric pressure, and weighing errors on the reproducibility of the test were studied. The inhibition factors for divinylacetylene, hydroquinone, *p-tert*-butylcatechol, and diphenylamine were determined. A second test in which 20 g. of monomer and 0.400 g. of benzoyl peroxide are brought to a spontaneous boil in a round-bottomed flask heated with a Glas-Col mantle was also developed. However, the sensitivity of this test to inhibitors and stabilizers was much lower than that of the test tube test.

A search of the literature and inquiries to several manufacturers of methyl methacrylate failed to uncover an activity (polymerization) test suitable for commercial use. To be satisfactory, the test must be relatively simple, must be reproducible to within 1–2%, and must give reasonable differences in values due to the variation in the concentration of inhibitors and stabilizers present in the monomer. Such tests already exist for vinyl acetate.[1] Attempts were, therefore, made to adapt these tests to methyl methacrylate.

Test Tube in Bath Test

As in the case of vinyl acetate, the simplest system appeared most likely to give the best results. Hence, methyl methacrylate was polymerized in bulk, purified benzoyl peroxide being used as catalyst. To make the test as sensitive as possible to inhibitors and stabilizers, the lowest temperature and lowest catalyst concentration consistent with adequate reproducibility had to be used. Hence, the effect of temperature and catalyst concentration on reproducibility were studied. Preliminary experiments indicated at once that a spontaneous boil could be obtained only by using bath temperatures close to the boiling point of methyl methacrylate. Therefore, only temperatures from 95.9 to 101.2°C. were studied extensively. From the results given in Table I, it will be seen that the percentage standard mean deviation for a given concentration of benzoyl peroxide decreased with increase in temperature. Thus, since a

TABLE I
Effect of Temperature and Catalyst Concentration on Reproducibility of Test[a]

| Sample no.[b] | Bath temp. (corr.), °C. | Wt. Bz₂O₂, g. | No. of tests | Time to boil, sec. | | |
				Arith. avg.	Standard Mean deviation	% Deviation
1	96.9	0.0300	8	536	25.2	4.7
2	98.9	0.0300	8	366	12.3	3.36
3	101.2	0.0300	8	353	7.9	2.24
1	95.9	0.0400	8	449	16.8	3.75
2	97.1	0.0400	6	364	13.7	3.76
2	98.9	0.0400	6	323	8.5	2.63
4	101.2	0.0400	4	286	5.45	1.91
5	101.2	0.0400	6	292	5.77	1.98

[a] In each test, 10 ml. of methyl methacrylate was polymerized in a test tube.

[b] Samples were commercial monomer obtained from three different manufacturers. They were goose-necked under vacuum prior to use in order to remove the inhibitor.

percentage deviation of 2% was considered just within acceptable limits, a temperature of 101.2°C. was chosen.

The effect of catalyst concentration on reproducibility was studied more extensively at 101.2°C. From the results given in Table II, it is apparent that the percentage standard mean deviation decreases as the amount of catalyst is increased up to 0.0400 g. until a minimum value of about 1.9% is reached. Amounts of catalyst greater than 0.04 g. will only decrease the sensitivity of the test to inhibitors and stabilizers and hence are undesirable. A polymerization temperature of about 101°C. and a catalyst concentration of 0.0400 g. in 10 ml. of monomer were, therefore, adopted for the test.

TABLE II
Effect of Catalyst Concentration on Reproducibility of Test[a]

| Sample no. | Wt. Bz₂O₂ g. | No. of tests | Time to boil, sec. | | | Barometric pressure, mm. Hg |
			Arith. avg.	Standard mean deviation	% Deviation	
3	0.0100	4	805	141	17.5	766
3	0.0200	6	467	13	2.8	764
3	0.0300	9	353	7.9	2.24	764
3	0.0400	10	305	5.8	1.90	764
2	0.0500	9	289	5.4	1.86	

[a] In each test 10 ml. methyl methacrylate was used.

Sensitivity of Test

To determine if the test had reasonably good sensitivity to known inhibitors and stabilizers, several compounds were studied. Time–concentration curves were obtained and the inhibition factor was calculated in the same manner as in the previous investigation on vinyl acetate.[1] The

results in Table III indicate that the test has considerable sensitivity, although concentrations of hydroquinone below 5 ppm cannot be detected.

TABLE III
Inhibition Factors of Various Compounds[a]

Inhibitor or stabilizer	Inhibition factor, sec./ppm	Concentration, ppm
Divinylacetylene	0.26	0–1160
Hydroquinone	1.4	78
	0.64	625
p-tert-Butylcatechol	0.46	625
Diphenylamine	0.50	625

[a] Test run according to recommended procedure.

Sources of Error

Effect of Oxygen. Since it has been established that oxygen is usually an inhibitor for the polymerization of methyl methacrylate,[2–8] a study was made to determine the magnitude of its effect under our experimental conditions. A sample was, therefore, treated in four different ways and the activity test run after each treatment.

A. The sample was blown with air for 1–2 hr. and was thus saturated with air at 25°C. The test was also carried out under an atmosphere of air.

B. The sample was stored at −70°C. in the solid state and melted just prior to the test. This sample, therefore, contained a small amount of dissolved air. Almost all of the samples in this investigation were treated in this manner. The test was done under air.

C. The sample was blown with hydrogen for nearly 2 hr. and the test was then done under air. Therefore, it contained only a trace of air due to its redissolving from the atmosphere during the test.

D. The sample was cooled to −78°C., the test tube evacuated, and the apparatus filled with hydrogen. This sample, therefore, contained only minute traces of dissolved oxygen.

The results are summarized in Table IV. These experiments were carried out at 95.9°C., at which temperature the effect of oxygen is probably somewhat greater than at 101.2°C. The difference between experiments A and C gave the maximum possible inhibition due to air, i.e., 21 sec. or 4.7%, assuming that the test would be carried out under air. The difference between experiments B and C gave the effect of the amount of air which is ordinarily dissolved in the sample, i.e., 3 sec. or 0.7%. The difference between experiments C and D gave the effect of the oxygen which redissolves in the sample from the atmosphere during the test, i.e., 0.7%. Varying amounts of dissolved air are thus potentially a major source of deviation. It was noted that the percentage standard mean deviation was lowest in experiment A, a little higher in experiment D, and substantially

higher in experiments B and C. Thus, there appears to be a definite indication that varying amounts of dissolved air are responsible for some of the deviation in results. To keep this deviation below 2%, it is thus necessary to use either freshly distilled monomer or freshly melted monomer which has been stored at −60 to −70°C. By observing these precautions, the very time-consuming operation of evacuating the test tube and filling it with hydrogen can be avoided. If, however, the percentage standard mean deviation due to all factors must be kept to values substantially below 1.9%, then operation under oxygen-free conditions is mandatory.

TABLE IV
Effect of Oxygen on Time to Reach a Spontaneous Boil [a]

Experiment	Atmosphere	No. of tests	Time to boil, sec. (Arith. Avg.)
A	Air	4	467
B	Air	8	449
C	Air	11	446
D	H_2	7	443

[a] In each experiment, 10 ml. of methyl methacrylate, 0.0400 g. of benzoyl peroxide, and a bath temperature of 95.9°C. were used.

Effect of Barometric Pressure. A statistical study of the effect of barometric pressure on a large number of samples of vinyl acetate has suggested that there might be a very small effect. A study of a few samples of methyl methacrylate has failed to reveal any effect. The magnitude of the deviation due to this factor can, therefore, be safely assumed to be only a minor fraction of the total.

Effect of Errors in Weighing the Benzoyl Peroxide. The benzoyl peroxide was usually weighed on a piece of aluminum sheet bent in the shape of a scoop which fitted into the top of the test tube. To determine if errors in weighing and losses in transferring were responsible for deviations, a comparison between the three following methods was made.

A. A 0.0400 g. portion of benzoyl peroxide was weighed in an aluminum scoop and transferred to the test tube; 10 ml. of monomer was then added.

B. A 1-ml. portion of stock methyl methacrylate, which contained benzoyl peroxide at a level of 0.0400 g./ml. and which was stored in a brine bath, was added to 9 ml. of monomer. The mixture was warmed to 25°C. and the test run in the usual way.

C. A 10 ml. portion of a stock solution of methyl methacrylate which contained benzoyl peroxide at a level of 0.0400 g./10 ml. and which was stored in a brine bath was warmed to 25°C. and the test run in the usual way.

The percentage standard mean deviation was slightly lower with method A than with B or C. Thus, the deviations due to errors in weighing the catalyst were probably negligible, since pipetting errors in experiment B

were only a few tenths of 1% and in experiment C they were of no consequence at all, since the ratio of monomer to catalyst always remained constant.

Effect of Fluctuation in Temperature. The fluctuation in the temperature, as measured with a Beckmann differential thermometer, rarely exceeded ±0.02°C. From the known effect of temperature on the rate of chemical reactions in general, 0.02°C. should cause a negligible deviation in results. To further confirm this point, 10 ml. of Pentasol acetate was added to the test tube and the time–temperature curve obtained. The curve was found to be quite reproducible when a 50–50 mixture of ethylene glycol in water was used as the bath liquid. In the preliminary experiments, a water bath covered with Nujol or Dow-Corning Anti-foam A was used, but the test tubes often became coated on the outside with the Nujol or Anti-foam and the heat transfer decreased substantially. A time–temperature curve was also obtained for methyl methacrylate, and the results are given in Table V.

TABLE V

Time versus Temperature during Polymerization of Methyl Methacrylate with Bath at 101.2°C. [a]

Time, sec.	Temp. of MMA, °C.
0	25.5°
60	84.5
120	99.4
180	106.3
240	110.0
300	113.8
324	116.5–118.5[b]

[a] Test was run according to recommended procedure.
[b] Spontaneous boil.

Recommended Procedure

The monomer is freshly distilled through a short column under reduced pressure. If it cannot be used immediately, it should be stored at −60 to −70°C. and melted 0–2 hr. before using. The test tubes must not have any scratches or lines made in manufacture, since these cause premature bubbling and give erratic results. The benzoyl peroxide must be purified by reprecipitation. (A filtered, saturated solution of the peroxide in C.P. chloroform is poured into 3 or 4 times as great a volume of filtered C.P. methanol.)

Reprecipitated benzoyl peroxide (0.0400 g.) is placed in a test tube (150 mm. × 22–23 mm. I.D., with a wall thickness of about 1.2 mm.) and 10 ml. of the monomer is pipetted in. A glass tube (250 mm. × 10 mm. I.D.) fitted with a cork is attached to the test tube to prevent contamination of the sample. The entire assembly is gently shaken to dissolve the catalyst and immediately placed in an insulated bath (50–50 ethylene

glycol–water) which is maintained at 101.2 ± 0.02°C. by means of a Bronwill constant temperature circulator. The position of the test tube is adjusted so that the top of the sample is about 1 in. below the surface of the bath liquid. A small lamp is placed behind the test tube to give illumination. The time required for the sample to come to a spontaneous boil from the instant it is placed in the bath is recorded. The boil should be sharp. A series of small bubblings may be due to specks of dirt, imperfectly cleaned glass surface, imperfections in the glass, or impurities in the catalyst. The test tubes are preferably cleaned with acetone, followed by chromic acid and water. They should then be rinsed with acetone, blown with a hair dryer, put in an oven at 110°C., and cooled to room temperature just before using.

Glas-Col Mantle Test

These experiments were carried out in a round-bottomed flask heated by a mantle. When the same procedure and the same amounts of methyl methacrylate (20 g.) and benzoyl peroxide (0.400 g.) as was used for vinyl acetate[1] were used, no spontaneous boil was obtained. Reducing the pressure down to 100 mm. Hg (abs.), varying the time of heating to give the first drop of condensate from 100 to 214 sec., and varying the boiling time from 15 to 60 sec. also failed to give a spontaneous boil. However, when the initial boiling step was eliminated, a spontaneous subsequent boil was obtained. (Actually, the sample boiled for 1–2 sec., since this is the time required to remove the mantle and start the watch.)

The procedure was as follows. Reprecipitated benzoyl peroxide (0.400 g.) was placed in a very clean 100 ml. Corning Pyrex, round-bottomed flask (capacity 125 ml.) with a female 24/40 standard tapered joint. Then 20 g. (21.4 ml.) of methyl methacrylate was pipetted in. The flask was shaken to dissolve the peroxide, and a Liebig condenser, filled with water at room temperature was attached. The mantle was preheated for 45 sec. and placed under the flask. The voltage on the mantle was adjusted beforehand so that the heat supplied would cause the first drop of condensate to fall in 115 ± 2 sec. When the first drop of condensate fell, the stop-watch was started and the mantle quickly removed. An empty beaker was placed around the flask to shield it from air drafts. The watch was stopped when the monomer reached a spontaneous boil.

The effect of oxygen on the test was studied by evacuating the air and filling the apparatus with hydrogen. No measurable effect was detected.

The percentage standard mean deviation was less than 0.5%. However, the sensitivity was much less than in the test tube test described previously. Samples of methyl methacrylate from three manufacturers gave 63.5, 71–73, and 72–73 sec., respectively. When 200 ppm of hydroquinone were added, the retardation of the spontaneous boil was only 15 sec. The inhibition factor was thus 0.075 sec./ppm. Since this inhibition factor is only 9% of that obtained with the test tube test, this test is obviously very

much less sensitive to inhibitors and stabilizers. This is primarily due to the very much higher catalyst concentration.

References

1. Georgieff, K. K., and G. S. Shaw, *J. Appl. Polymer Sci.*, **5**, 212 (1961).

2. E. I. du Pont de Nemours and Co., *Ind. Eng. Chem.*, **28**, 1160 (1936).

3. Dittmar, H. R., U. S. Pat. 2,373,464, to E. I. du Pont de Nemours and Co. (1945).

4. Bovey, F. A., and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948).

5. Rutovskiĭ, B. N., and G. S. Goncharov, *Zh. Priklad. Khim..*, **26**, 426 (1953); *Zh. Obsheh. Khim.*, **26**, 389 (1953).

6. Schulz, G. V., and G. Henrici, *Makromol. Chem.*, **18–19**, 437 (1956).

7. Korchagina, E. P., *Uch. Zap. Sartovsk. Gos. Univ.*, **71**, 13 (1959).

8. Ashikari, N., *Bull. Chem. Soc. Japan*, **32**, 1056 (1959).

Résumé

Afin de déterminer industriellement la pureté du méthacrylate de méthyle, on a mis au point deux tests d'activité (de polymérisation). Dix ml de monomère sont chauffés en présence de 0.04 gr de peroxyde be benzoyle dans un tube à essai, plongé dans un bain à 101.2° jusqu'à ébulition. On étudie l'effet de la température, de la concentration en catalyseur, de l'oxygène, de la pression atmosphérique, et des erreurs de pesée sur la reproductibilité de l'essai envisagé. On détermine les facteurs d'inhibition pour le divinylacétylène, l'hydroquinone, le *p-tert*-butylcatéchol et la diphénylamine. On expose également un second test dans lequel 20 g. de monomère et 0.400 g. de peroxyde de benzoyle sont portés à ébulition dans un ballon à fond rond chauffé par un manteau de verre (glas-Col). Cependant, la sensibilité de ce second essai est plus faible vis-à-vis des inhibiteurs et des stabilisateurs que le test en tube à essai.

Zusammenfassung

Zwei Aktivitäts-(Polymerisation)-tests zur technischen Ermittlung der Reinheit von Methylmethacrylat wurden entwickelt. Zehn ml des Monomeren werden mit 0,0400 g Benzoylperoxyd in einer in ein Bad von 101,2° eingetauchte Eprouvette erwärmt, bis spontanes Sieden eintritt. Der Einfluss von Temperatur, Katalysatorkonzentration, Sauerstoff, Luftdruck und Wägefehlern auf die Reproduzierbarkeit des Tests wurden untersucht. Die Inhibierungsfaktoren von Divinylacetylen, Hydrochinon, *p-tert*-Butylbrenzkatechin und Diphenylamin wurden bestimmt. Weiters wurde ein zweiter Test entwickelt, bei dem 20 g Monomers und 0,400 Benzoylperoxyd in einem mit einem Gals-Col-Mantel erhitzten Rundkolben zum spontanen Sieden gebracht werden. Die Empfindlichkeit dieses Tests gegen Inhibitoren und Stabilisatoren war aber bedeutend geringer als die des Eprouvettentests.