

Polymerization of Methyl Methacrylate by Catalyzed Peroxide Decomposition Without Applied Heat

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Synopsis

The exotherm for the polymerization of methyl methacrylate was monitored by a simple thermal technique to gain useful information about the effect of several factors on the polymerization rate and the degree of completion. All reactions were begun at room temperature (24°C) and no external heating was provided. Initiation was by decomposition of benzoyl peroxide (and mixtures with lauroyl peroxide) catalyzed by the accelerator N,N-dimethyl-*p*-toluidine. Specific factors examined were peroxide and accelerator levels, sample size, peroxide combinations, and crosslinking agents. The results are discussed in terms of the stoichiometry of the initiator system; the balance of heat generation, heat capacity, and heat loss; and the autoacceleration effect.

INTRODUCTION

Frequently polymers are formed into specific shapes by a procedure wherein a monomer or prepolymer is polymerized in place, which is sometimes referred to as casting. Examples include various coatings, fiber glass constructions, embedding techniques, etc. A number of complex initiator formulations are employed for each monomer system and their selection is based on use experience. Often in this procedure the polymerization must start at ambient temperature or a little above, although owing to the exothermic reaction it will subsequently rise well above this level. The reaction occurs under very complex and varying conditions as opposed to the rather well-controlled conditions that prevail in most commercial reactors where large quantities of polymers of consistent quality are made. Kinetic data for the latter may be obtained and expressed in a fundamental fashion and are often utilized quantitatively. Kinetic data would also be valuable for casting procedures; however, there is little chance of obtaining fundamental data nor of using it quantitatively since the complex features are an inherent part of the process and must be preserved. There is a considerable need, however, for data of some type to assist in the decision-making process where the types and levels of initiators, accelerators, and other agents are selected.

This study was undertaken because of a need for this type information in connection with our work on developing polymeric surface treatments for

concrete, concrete crack repair systems, and other technology associated with the concept of impregnating the pores of concrete with liquid monomers with subsequent conversion to polymer.¹⁻⁵ We have developed a simple thermal analysis technique to follow the exotherm of the polymerization reaction which allows rather rapid screening of various systems. Some results of general interest are reported here. The monomer employed was methyl methacrylate, MMA, with benzoyl and lauroyl peroxide as initiators in conjunction with the accelerator *N,N*-dimethyl-*p*-toluidine.

BACKGROUND

The basic reactions of peroxide decomposition⁶ and polymerization of MMA⁷ have been thoroughly characterized for isothermal conditions. However, the casting process of interest here is by necessity nonisothermal, and usually some agent is added to accelerate the decomposition of the peroxide.⁶ Some tertiary amines are quite effective at catalyzing this decomposition. Numerous fundamental studies to ascertain the mechanism and kinetics of this action have been reported,⁸⁻¹⁵ but still the picture is not entirely complete. To circumvent the complexities and yet provide useful information, less fundamental approaches are generally employed. An example is provided by the work of Brauer et al.,¹⁶ who utilized an ultrasonic viscometer to track the progress of MMA polymerization produced by benzoyl peroxide decomposition catalyzed by various amines. Their tests were carried out on test tube samples immersed in a bath held at either 21° or 37°C. Noller et al.¹⁷ employed a somewhat different approach in that they followed the temperature of the reaction mixture after immersing it in a bath held at various elevated temperatures (65°-145°C), which is a standard SPI procedure.¹⁸ They studied the effect of various accelerators and inhibitors on the peroxide curing of polyesters. Their results are presented in terms of the useful concept of the so-called "kick-off" temperature.¹⁸ A great deal of work has been done in the field of dentistry with MMA systems to develop self-curing acrylic resins for a variety of dental uses.¹⁹⁻²³ Most of these systems begin with a syrup of acrylic polymer dissolved in MMA with the ambient conditions maintained at body temperature.

All of the literature mentioned above and much not mentioned is very useful; however, it fails to consider some effects and specific systems of interest to us, as will be described.

EXPERIMENTAL PROCEDURE

The exotherm was followed as a key to the polymerization rate. In such cases, the sample size and thermal environment are very important factors which must be carefully controlled and designed if the results are to be reproducible and to duplicate enduse conditions. Often these factors are not even mentioned in the literature. We wished to construct a system of measurement that simulated in some way our enduses that gave repro-

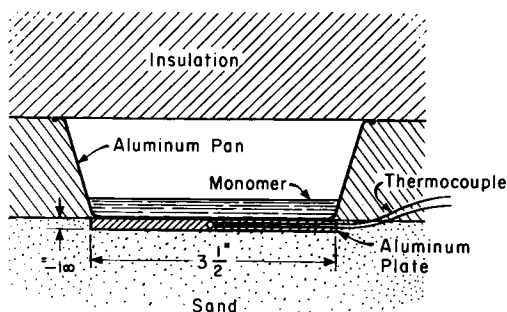


Fig. 1. Thermal apparatus for following polymerization exotherm.

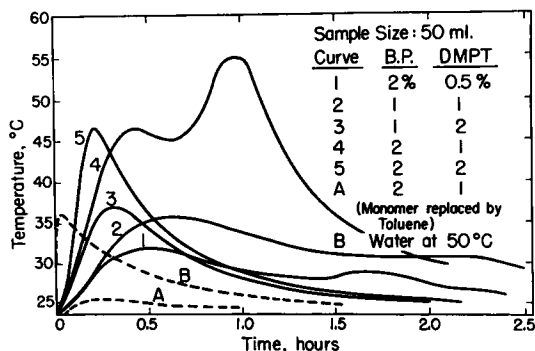
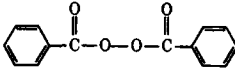
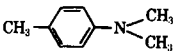


Fig. 2. Curves 1-5 show exotherm for MMA using indicated peroxide and accelerator levels in weight per cent. Curve A shows heat generation by initiator system when there is no polymerization. Curve B illustrates cooling characteristics in the absence of heat generation.

ducible results and where the thermal balance could be easily varied. The system adopted is shown schematically in Figure 1. It consists of an aluminum plate resting on a bed of sand. A disposable aluminum pan is placed on this plate, and it is here where the reaction takes place. A thermocouple to measure the temperature rise is embedded in the aluminum plate. The insulation shown was installed to reduce evaporation and spurious air currents, and to duplicate conditions where heat loss from above is not large.

The apparatus and monomer mixture were initially at room temperature (24°C) in all experiments. The monomer and initiator system was introduced into the pan at time zero, after which the temperature reading of the thermocouple was followed by a recording potentiometer to produce data such as shown in Figures 2, 3, 4, 5, and 7. The peroxide was dissolved in one half of the monomer and the accelerator in the other half, and the two halves were mixed together in the pan. An idea of the heat capacity and heat loss characteristics of the system are provided by the dashed curve B in Figure 2 where warm water at 50°C was poured into the pan. The thermocouple indicated a maximum temperature of 36°C reflecting the

TABLE I
Materials

Name	Abbreviation	Structure	Source and and purity
Methyl methacrylate	MMA	$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{COOCH}_3$	Rohm and Haas 10 ppm MEHQ*
Trimethylolpropane trimethacrylate	TMPTMA	$(\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{COOCH}_2)_3-\text{CCH}_2\text{CH}_3$	Rohm and Haas 96% 200 ppm MEHQ
Benzoyl peroxide	BP		Reichhold 96%
Lauroyl peroxide	LP	$\text{CH}_3(\text{CH}_2)_{10}\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_{10}\text{CH}_3$	Reichhold 96%
N,N-Dimethyl- <i>p</i> -toluidine	DMPT		Eastman

* MEHQ = Monomethyl ether of hydroquinone.

system thermal capacity and then declined owing to heat loss from the pan and plate. Data of this type could be employed to extract thermal parameters for use in mathematical models of the process if desired. The system can also be altered to match the thermal characteristics of a specific application.

The positioning of the thermocouple in the plate has the advantage of not having to recover or replace it after every experiment plus an assurance of reproducible positioning. However, it also raises the question of how its reading would correlate with that of a thermocouple placed directly in the monomer. Several experiments were run to check this, and it was found that the two temperatures did not vary by more than 5°C and the time characteristics were always identical.

The principal materials employed here are given in Table I along with abbreviations, structure, sources, and purity. In several cases the inhibitor was removed from MMA, but this did not alter the experimental results in any significant way. No effort was made to exclude or remove dissolved oxygen from the monomer to preclude the possibility of oxygen inhibition since generally in casting practice oxygen cannot be avoided. The problem does not seem to be severe with methyl methacrylate and is not regarded as a major factor in any of the data that follow.

EFFECT OF BENZOYL PEROXIDE AND DMPT CONCENTRATION

We wished to explore the various types of accelerators that might be used in conjunction with benzoyl peroxide to effect a polymerization of MMA starting at 24°C with no external thermal assist, and then to optimize the composition of accelerator and peroxide for rapid and complete cure. Preliminary experiments revealed that N,N-dimethyl-*p*-toluidine (DMPT)

was a far more effective accelerating agent than dimethylaniline, triethanolamine, and benzenethiol which produced some polymerization and diethylaniline, cobalt naphthenate, tributylamine, and triethylamine which produced no polymerization. These observations are consistent with previous observations where available.¹⁷ Subsequent to this, our entire efforts were directed toward the use of DMPT.

Figure 2 shows results for polymerizing MMA with various levels of BP and DMPT at a fixed sample size of 50 ml. Each curve shows a rapid rise in temperature which peaks out in about 12 min for curve 5 but in about 30 min for curve 1. For curve 4 there is a very pronounced second peak which occurs after about 1 hr. There is a less exaggerated second peak for curves 1 and 2 appearing at longer times.

Curve A was generated by replacing MMA with toluene so that no polymerization would take place while we examined the weaker exotherm for the decomposition of the peroxide. There is a small temperature buildup that peaks a little sooner than the first peak in the polymerization curves and then falls off slowly. We can thus attribute the first peak in curves 1-5 to the nature of the rise and subsequent fall in the number of free radicals made available by the initiator system for polymerization since curves 1-5 are roughly amplifications of A in this region. However, the second peak is more complex in origin, and more will be said about it later.

The slopes prior to the first peak depend on the concentration of BP and DMPT in a fashion easily reconciled with fundamental kinetic data.^{10,11} The latter indicate the rate of radical generation to be proportional to $[BP][DMPT]$, and thus polymerization rate is proportional to the square root of this product. Curves 1 and 2 have the same slope and the same concentration product of 1 ($\%$)², while curves 3 and 4 have the same slope and the same concentration product of 2. The experimental slopes increase as the product of concentrations increase. According to the fundamental studies, the peroxide and amine react in equimolar proportions, and this would then be the most efficient proportion in which to combine them. This is borne out here in that a weight ratio (BP/DMPT) of 2 corresponds very nearly to equimolar proportions.

In addition to the curves generated, it is very important to examine the nature of the product to gain some idea of the extent and quality of the cure. In the present case, the best product was made under the conditions of curve 4. It appeared to be completely polymerized, while the next best (curve 2) was tacky on the surface. Condition 5 gave a thick syrup, while those produced under conditions 1 and 3 were only low-viscosity liquids after 2 hr but became syrups overnight. The second peak seems to be needed for good cures. All samples were reddish brown in color.

The reproducibility of the thermal data was quite good. Each curve in Figure 2 was repeated at least four times with excellent duplication, except that the magnitude of the second peak in curve 4 did vary somewhat. The quality of the cure was directly related to the strength of this peak.

EFFECT OF THE BALANCE OF HEAT GENERATION, HEAT CAPACITY, AND HEAT LOSS

In the apparatus shown in Figure 1, the ability to lose heat, or the heat transfer coefficient, is effectively independent of the sample size. However, the ability to generate heat and the heat capacity are directly proportional to the sample size. Thus, by changing the sample size this balance is altered, and as a result the temperature rise will be changed. This will affect the polymerization rate and the quality of the cure. Figure 3 shows results for adding different quantities of MMA (plus 2% BP and 1% DMPT) to the pan. The first peak appears at roughly the same time for each curve; however, it is diminished in magnitude for smaller samples as may be expected from the reduced potential for heat generation. Of more interest is the effect on the second peak. At 60 ml and above, it does not occur. It is most exaggerated for 40 and 50 ml, but falls off in intensity and is shifted to longer times as the sample size is reduced. The 80-ml sample was a thick syrup at the end of 2 hr, while the 20-ml sample had a hard core and the 60-ml sample was hard with a tacky surface. The 40- and 50-ml samples were thoroughly cured, but the 30-ml sample had a syrupy layer on top and the 20-ml sample was syrupy throughout. It is thus evident that there is an optimum heat balance determined by sample size. This is probably true for all systems, with the optimum depending on the details.

The fate of a too thick specimen may be speculated as follows. As the reaction starts, high temperatures are generated because of the large heat generation with a large sample which leads to even higher rates. During this period, only short chains are formed and the peroxide is used up early because of the high temperature. Virtually no peroxide is left for completion of polymerization, so the reaction dead-ends²⁴ with an incomplete cure.

In thinner specimens, the balance of heat generation and loss is such that the system never attains a sufficient kick-off temperature to maintain its momentum, so the reaction dies. That is, as time goes on, the initial high rate of reaction decreases owing to diminished peroxide and monomer concentration and the temperature never becomes high enough to keep it going.

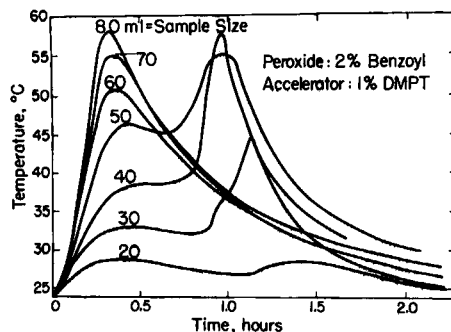


Fig. 3. Effect of sample size on the nature of the exotherm.

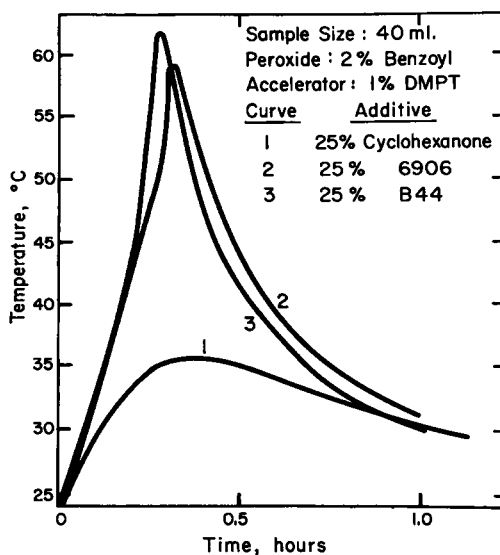


Fig. 4. Effect of nonreactive additives on the exotherm. The additive for curves 2 and 3 are polymers.

Another approach to this balance is provided by increasing the system heat capacity, i.e., energy needed to effect a unit increase in temperature, without a corresponding increase in potential for heat generation. This was accomplished here by adding sand to the pan. As the reaction proceeds, the sand must be heated up as well as the polymer-monomer mixture. As the proportion of sand was increased in a series of experiments, the maximum temperature attained declined as expected, and eventually an incomplete cure resulted since the reaction was not self-sustaining.

A somewhat similar circumstance occurs in the curing of systems in which a substantial amount of polymer is initially dissolved in the monomer to make a syrup, as is done in dental systems. The polymer is unreactive in this case in contrast to polyesters and has the same effect on the heat capacity as adding sand. Added polymer, however, does not seem to reduce the degree of cure; in fact, it speeds it up. This situation was simulated here with the results shown in Figure 4. Curves 2 and 3 are for cases where 25% by weight of acrylic polymers were dissolved in the monomer prior to introducing the mixture to the pan and adding BP and DMPT. The polymer designated as 6906 is a low molecular weight (5000 to 8000) acrylic with $T_g \approx 90^\circ\text{C}$, while the B44 is of higher molecular weight (80,000) with $T_g = 60^\circ\text{C}$. Both were obtained from Rohm and Haas and are experimental acrylic copolymers. The magnitude of the first peak ($\sim 60^\circ\text{C}$) in both cases is significantly greater than that for corresponding sample sizes in Figure 3 ($< 40^\circ\text{C}$), even though the potential for heat generation is less by 25%. Both products were completely cured in 1 hr. Another experiment was run in which an unreactive solvent, cyclohexanone, was substituted for the polymers (see curve 1). This peak is lower than the

corresponding one in Figure 3, thus reflecting the higher heat capacity. The difference can be explained by the possibility of autoacceleration, or the Tromsdorff effect.²⁵ The presence of polymer increases the polymerization rate owing to the decrease in the termination rate constant brought about by diffusion control that occurs when the viscosity becomes large. The solvent does not produce this increase in viscosity; in fact, it will reduce it. From this we can see that the formation of polymer in addition to the heat balance will influence the polymerization rate.

It is now possible to speculate on the origin of the second peak observed. The first peak occurs because of the initial high rate resulting from the high concentration peroxide, accelerator, and monomer and the subsequent decline in rate as these concentrations are diminished. In many cases this decline will occur at such a rate as to result in an incomplete cure. With polymer present initially, this peak is exaggerated sufficiently by autoacceleration to give a complete cure by itself. However, in some cases of critical size with a proper initiator system, enough polymer may be formed by the time the rate decline starts so that autoacceleration becomes appreciable and the rate will pick up again and a complete cure will result. This situation requires a very delicate intersection of events and could easily be missed or not occur at all.

The conditions for attaining good cures starting from low temperatures are complex, and it is not surprising that general rules for assuring them are not available. Each system must be tested individually, and the physical factors must closely duplicate those of the intended application or false conclusions will be reached. A principal point here is that the exotherm is not just a consequence of the polymerization but is in fact necessary to ensure that polymerization will occur. High heat losses, high heat capacities, and low heat generation may prevent curing and thus preclude utilization of this approach in certain systems when external heating is not used. The only solution in these cases is to raise the system temperature. Most of the available literature does not point this out, and critical information relating to the conditions of experimental data is absent.

EVALUATION OF BENZOYL AND LAUROYL PEROXIDE COMBINATIONS

In an effort to develop initiator systems with more flexibility than can be achieved with simply BP and DMPT, combinations of peroxides were examined. Figure 5 shows some results for fixed levels of LP and DMPT with varying amounts of BP. In the absence of an accelerator, lauroyl peroxide decomposes more rapidly than benzoyl²⁶; however, DMPT has very little catalytic effect on it.¹⁷ Thus, in the presence of DMPT, benzoyl is a more active peroxide than lauroyl, which can produce interesting and useful results. In Figure 5, the extreme left curve represents the same system explored in Figure 3, except for the presence of 2% LP. This curve is of similar shape, but somewhat higher temperatures are achieved (the effect

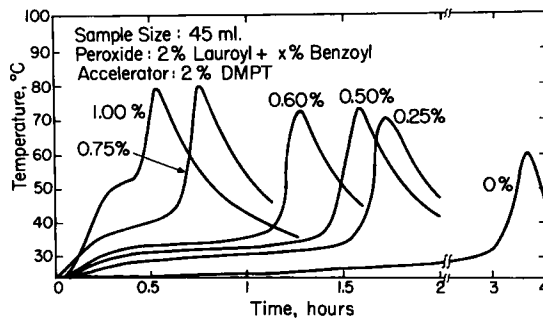


Fig. 5. Polymerization of MMA using peroxide combinations.

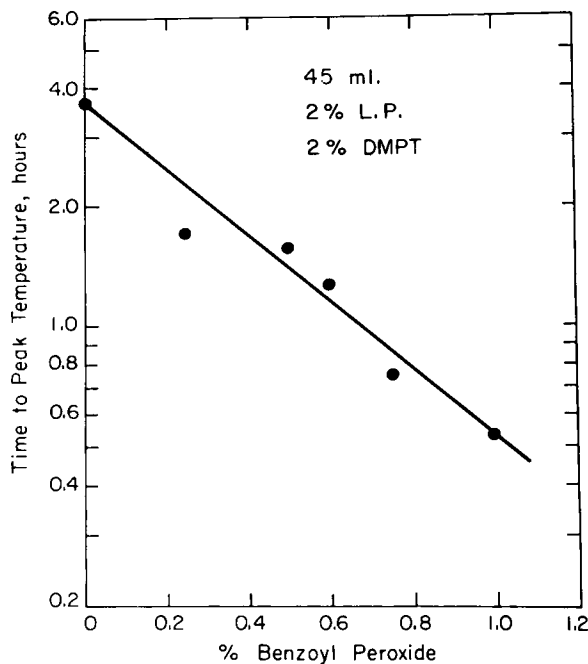


Fig. 6. Effect of BP level on the time to peak temperature. Data from Fig. 5.

of LP), and the first peak is now more of a shoulder. As the BP content is reduced, the first peak is further subdued; however, there is always a strong second peak which shifts to longer times. The time to the second or highest peak is shown versus BP level in Figure 6. This results in a very versatile system in which the pot life can be varied over wide ranges. The basic feature here is that the BP begins to decompose rapidly under the influence of DMPT and serves principally to raise the temperature to a level where LP can decompose readily (more or less unaided by DMPT), and it is the latter source of radicals that does the main job of polymerization.

In all cases a complete cure was developed. The samples were quite hard and only the one with 0% BP exhibited any tackiness. The tempera-

tures generated were considerably higher than in previous figures. A side effect of this was to create bubbles in the product owing to vaporization of the MMA.

EFFECT OF A CROSSLINKING AGENT

Multifunctional monomers or crosslinking agents are often added to cast systems to build up the molecular weight and to increase the polymerization rate. The former may be necessary to offset the tendency to form quite short chains at high polymerization rates. The effect goes beyond this usually to produce crosslinked networks. The increase in rate that generally occurs may be quite valuable in some cases, and it is this aspect that we wish to explore here. The crosslinking agent employed was TMPTMA (see Table I). Some thermal results for a fixed sample size and initiator system but varying levels of TMPTMA are shown in Figure 7

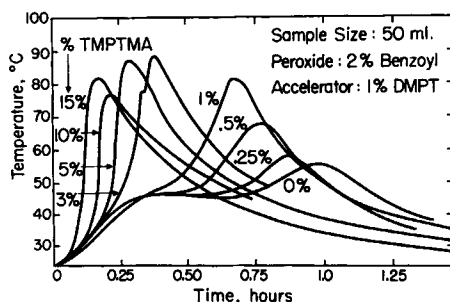


Fig. 7. Copolymerization of MMA with the crosslinking agent TMPTMA.

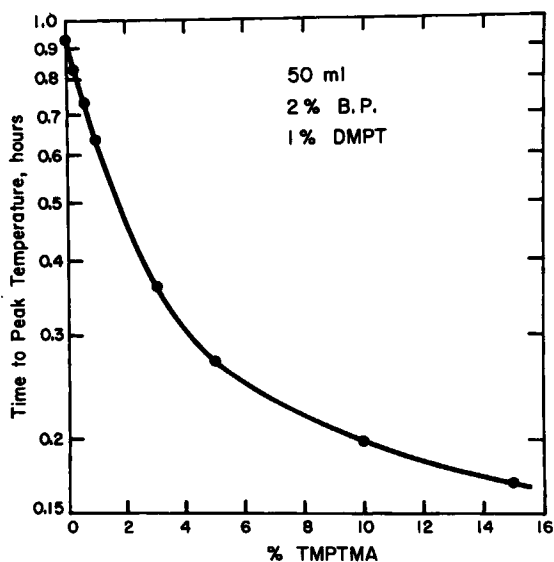


Fig. 8. Effect of TMPTMA level on the time to peak temperature. Data from Fig. 7.

(note the expanded time scale). As the proportion of this agent is increased, the second peak is increased in magnitude and shifted to shorter times to the point where it merges with or surpasses the first peak. Figure 8 illustrates the uniform shift of this peak. TMPTMA has a very profound effect on the polymerization rate, which in itself is quite useful.

All of the products were very hard, with no tacky surfaces. However, another effect is produced in the product by the crosslinking that occurs, viz., brittleness. The samples with the highest contents of TMPTMA were so brittle that they were cracked from thermal stresses. This problem diminished as the TMPTMA content was decreased.

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