

# Microwave Polymerization of Poly(methyl acrylate): Conversion Studies at Variable Power

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**ABSTRACT:** Methyl acrylate (MA) was polymerized by microwave radiation at three different powers, namely, 200, 300, and 500 W. The percentage conversion of the reaction was followed by Fourier transform infrared (FTIR) spectroscopy. The specimen temperature during the polymerization process was measured to select a suitable temperature for comparison with the conventional method. The results indicate that a similar comparable temperature of about 52°C was found for all the microwave power settings tested. The microwave polymerization process was compared with that of the thermal method at 52(±1)°C under comparable reaction conditions. The reaction rate enhancement of the microwave polymerization compared to the thermal method was found to be as follows: 275% for the 500 W, 220% for the 300 W, and 138% for the 200 W, indicating a significant correlation between the reaction rate enhancement and the level of microwave power used. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 787–797, 1997

**Key words:** microwave; polymer; poly(methyl acrylate); conversion; infrared spectroscopy

## INTRODUCTION

Industrial use of microwave radiation as an affordable alternative to thermal heating of the polymerization process has generated a lot of interest recently. The main advantages of microwave processing of materials are an increased rate of production, improved product characteristics, uniform processing, less floor space required, and convenience and controllability of the process.<sup>1</sup> Some of the applications of microwave dielectric heating include moisture analysis,<sup>2</sup> microwave catalysis,<sup>3</sup> wet ashing procedures of biological and geological materials,<sup>4</sup> and dissolution of ore samples.<sup>5</sup> The current debate on the alternative use of microwaves to conventional thermal heating has

focused on the involvement of a “specific microwave effect” other than the well-accepted dielectric heating. There are reports of various reactions that show similar kinetics under both microwave and thermal methods at comparable temperatures,<sup>6–13</sup> suggesting a simple dielectric heating of materials by microwaves. There are other reports, however, which show a clear reaction rate enhancement under microwave radiation compared to the thermal method at comparable reaction conditions,<sup>14–19</sup> indicating a “specific microwave effect” other than the dielectric heating. In the synthesis of refractory beta-branched amino acids, an enhancement of reaction rate was observed, which was attributed to the molecular stirring action caused by microwave dielectric heating.<sup>20</sup> Solid-state reactions involving diffusion of Pyrex<sup>TM</sup> glasses and ethylene oxide in PVC under microwave radiation also showed increased reaction rates possibly due to improved transport

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**Table I Reaction Rate Enhancement of Microwave Polymerization of PMMA and PS at Variable Power Compared to the Conventional Method Under Comparable Reaction Conditions**

Microwave Power (W)	Reaction Rate Enhancement	
	PMMA (%)	PS (%)
500	150	190
300	140	120
200	130	—

PMMA, poly(methyl methacrylate); PS, polystyrene.

properties.<sup>21,22</sup> Microwaves are also reported to show product selectivity in some Diels-Alder reactions,<sup>23</sup> dry organic reactions,<sup>24</sup> and cracking of certain industrial solvents.<sup>25</sup> Superior morphological properties have been reported for epoxy systems cured by microwave radiation.<sup>26,27</sup> Given the wide spectrum of results, which seems to differ in conclusion with regard to chemistry and kinetics, of reactions, the conclusion that microwave and thermally treated samples undergo similar chemical and kinetic mechanisms may be simplistic.

The thermal and nonthermal interaction of microwave radiation with materials has been reviewed in an earlier article.<sup>28</sup> The reaction rate enhancement of the microwave polymerization of methyl methacrylate (MMA)<sup>29,30</sup> and styrene,<sup>31</sup> compared to the conventional method at comparable reaction conditions, was determined and is shown in Table I. Also, the limiting conversion of the reaction varied for the microwave and thermal polymerization. The thermal polymerization of MMA at the comparative temperatures of 69, 78, and 88°C displayed a limiting conversion of about 90%, while the limiting conversion of the microwave method declined in the following order: 200 W, 88% > 300 W, 84% > 500 W, 78%. In the styrene polymerization, the limiting conversion showed a similar trend: 300 W, 72% > 500 W, 68%. The above work has now been extended to methyl acrylate with an objective to study the reaction rate enhancement of microwave polymerization and the trend in limiting conversion with variable microwave power and forms the basis of this article.

## EXPERIMENTAL

The methyl acrylate (MA) monomer of analytical grade was obtained from Fluka and distilled un-

der vacuum. The midfraction of the distillate was collected and stored under nitrogen gas in the freezer for not more than three days prior to use. The monomer was verified to be pure by <sup>1</sup>H-NMR spectroscopy. The initiator, azobisisobutyronitrile (AIBN), was purified by recrystallizing from methanol and stored in the freezer in dark for not more than five days. To prepare samples for polymerization, 4.1–4.2 mg of AIBN (0.85% by weight of the monomer) was taken in a 4 mL sample vial of 15 mm diameter, and 0.5 mL (478 mg) of MA was transferred into the glass vial under nitrogen gas using a hypodermic syringe. (The ratio of initiator to monomer is generally maintained at less than 1% by weight to avoid any undesired side reactions of the initiator, like recombination of the primary radicals, chain transfer reactions, etc.) Thereafter, the vial was closed with a screw cap under nitrogen gas and was subjected to either thermal or microwave polymerization. Each vial corresponded to one cure time for either thermal or microwave cure.

The microwave polymerization was conducted in a multimode microwave cavity. The microwave source was from a 2.45 GHz frequency magnetron powered by a 1.26 KW variable power generator, which could be operated at different power levels. To prevent formation of hotspots due to nonuniform heating, the cavity was designed with a rotating platform on which the sample could be placed. The microwave chamber temperature was measured by a stainless steel K-type probe (–200 to 1200°C). Other details of the microwave setup has been given in an earlier article.<sup>30</sup> As the temperature of the oven and that of the sample was different, the temperature of the sample was monitored separately. The sample temperature just after the microwave cure cycle was determined by inserting a thermocouple into the sample directly and immediately after the prescribed cure time. To minimize any cooling effect of the sample, the vial was placed in an insulating jacket during the temperature measurements, and the measurements were all taken in less than 30 s after the cure time. The thermal polymerization was conducted in a 1500 W thermal oven at preset temperatures. The temperature of the sample was measured after the specific time of cure by a thermocouple as described above and quenched in dry ice/acetone bath. The sample was then dissolved in 3.5 mL chloroform and analyzed by FTIR spectroscopy using a PE1650 FTIR spectrometer. The spectra for the liquid samples were obtained by using a KBr liquid cell with a path length of 0.1

mm. Each spectrum was averaged over 16 scans at  $4\text{ cm}^{-1}$  resolution. The absorbance peak area of the C=C bond of the monomer at  $1631\text{ cm}^{-1}$  was measured and used to determine the percentage conversion of the MA reaction.

The polymerization of MA has been reported to be highly nonreproducible<sup>32</sup>; therefore, not much work can be found in the literature. Hence, extreme care was taken during the sample preparation. To obtain reproducible data, the initial temperature of the microwave cavity was maintained at a constant temperature of  $30^\circ\text{C}$  to eliminate variation in the ambient temperature. The cavity was cooled to  $30^\circ\text{C}$  after every experiment before proceeding to the next experiment. During sample preparation, the initiator was exposed to room temperature for less than 30 min. Also, after mixing the reactants, the reaction mixture (MMA and AIBN) was immediately stored in the dry ice/acetone bath. Later, the reaction mixture was thawed to room temperature in less than 5 min before polymerization.

## RESULTS AND DISCUSSION

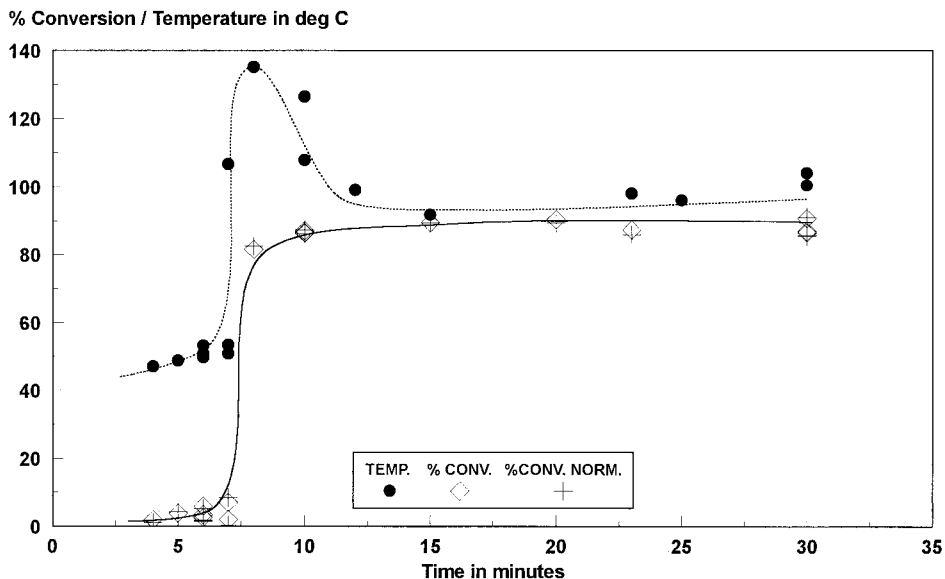
Vinyl polymerization processes involve changes in the C—C double and single bonds. It is therefore possible to follow the extent of the polymerization reaction by following the changes in these bonds. To offset any change in these IR bands due to either the concentration of the sample or due to spectrometer instability, an internal reference band is generally used to normalize the band being studied. In MA polymerization, the carbonyl functional groups does not participate in the reaction; therefore, the vibrational band at  $1731\text{ cm}^{-1}$  would be an ideal internal reference band. The carbonyl band, however, had a slight shift and change in intensity on polymerization. Gulari et al.<sup>33</sup> reported that assuming the spectrometer to be stable, monitoring only the integrated peak area of the double bond of MMA at  $1643\text{ cm}^{-1}$  introduced less total error compared to using an internal reference band. For this work, the stability of the spectrometer was verified by repeated scanning of the initial reaction mixture (0.5 mL of MA with AIBN) at zero time over several months of the project. An accurate spectra with the C=C mean peak area of 18.4 within a range of  $\pm 0.4$  was obtained. The normalized data using the carbonyl band as the internal reference band and the raw data of percentage conversion, however, were compared for the 200 W microwave

polymerization and is shown in Figure 1. The similarity in the data substantiates the irrelevance of internal reference band in the present study. The percentage conversion reported in this paper was therefore calculated using the integrated peak area of  $1643\text{ cm}^{-1}$  band alone.

### Microwave Polymerization of MA

The conversion and temperature profile during the microwave polymerization of MA at 200, 300, and 500 W is shown in Figures 1–3, respectively. The polymerization was characterized by a sudden acceleration in the rate of reaction at 5–9% conversion of the reaction, along with a corresponding increase in the specimen temperature. This phenomena has been previously observed and has been known variously termed as the Gel, Trommsdorf, Norrish Smith effect, and as the auto-acceleration of the reaction.<sup>34</sup> The gel effect in the thermal polymerization of MA has been reported to be very sharp, with the onset of the autoacceleration being from as early as 1–10% conversion of the reaction.<sup>32,35,36</sup>

Earlier reports indicate that while reproducible conversion data could be obtained before and after the gel effect, the gel effect itself was extremely sensitive due to the rapid reaction rate and the time taken to quench the reaction.<sup>37,38</sup> Reproducible data at the gel effect was therefore difficult to obtain. This would be true for all reactions characterized by the gel effect, including MA. In the 200 W microwave polymerization, the sensitive range was from 7–8 min, at which the reaction could be anywhere from the onset of the gel effect at 5–9% to the end of the gel effect at about 80% of the reaction. Similarly, the sensitive range in 300 and 500 W cure was from 4–5, and 3–4 min, respectively. Good reproducibility of the conversion of the reaction after the gel effect was observed, as indicated by the average percentage conversion for 500 W reaction at 7 min, to be 84.7% within a range of  $\pm 0.2\%$ . To determine a comparable temperature characteristic of the microwave cure, the specimen temperature just after completing the cure cycle was plotted against the cure time as shown by the dotted curves in Figures 1–3. The results show that the maximum of the exothermic peak was about  $135^\circ\text{C}$  for all three power settings. To provide a meaningful comparison, the temperature of the thermal curing reaction was set at the temperature just before the onset of the exothermic peak, which was about



**Figure 1** Conversion and temperature profile with time for microwave polymerization of MA at 200 W.

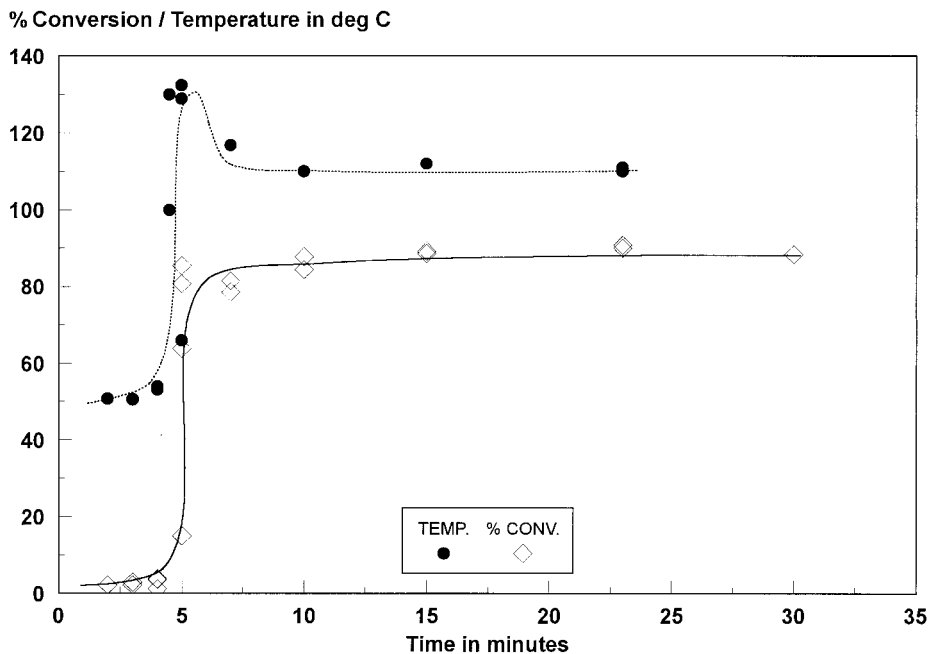
52°C for all the three power settings, as shown in Figure 4.

As discussed in our article on styrene,<sup>31</sup> The similar comparable temperature at different power settings may be due to microwave radiation at different power settings, attaining a similar energy with respect to the duration of irradiation.

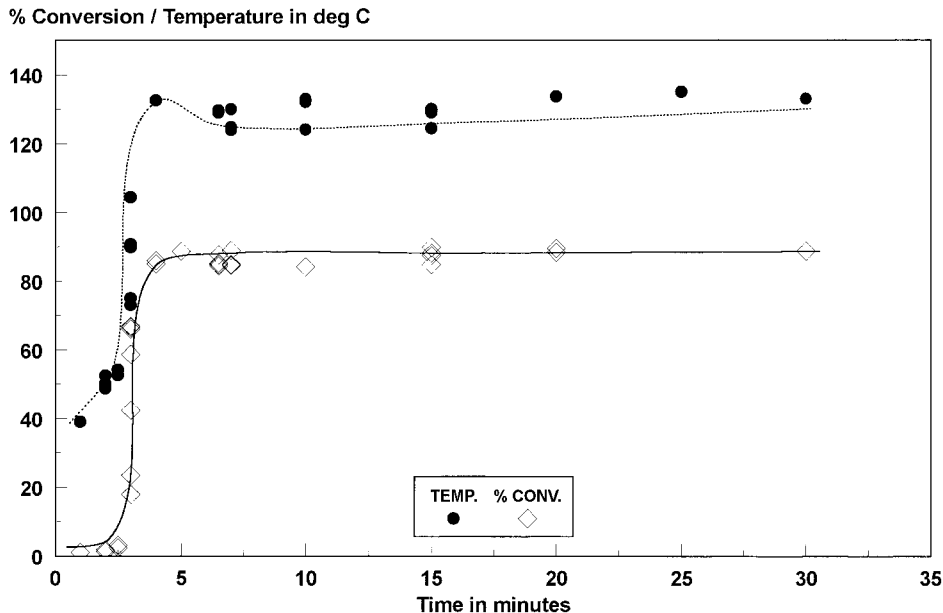
The heating rate of the sample under microwave radiation is governed by the following variables<sup>1,39-41</sup>:

$$dT/dt = P_d/C\rho \tag{1}$$

where  $T$  is the temperature of the heated material



**Figure 2** Conversion and temperature profile with time for microwave polymerization of MA at 300 W.

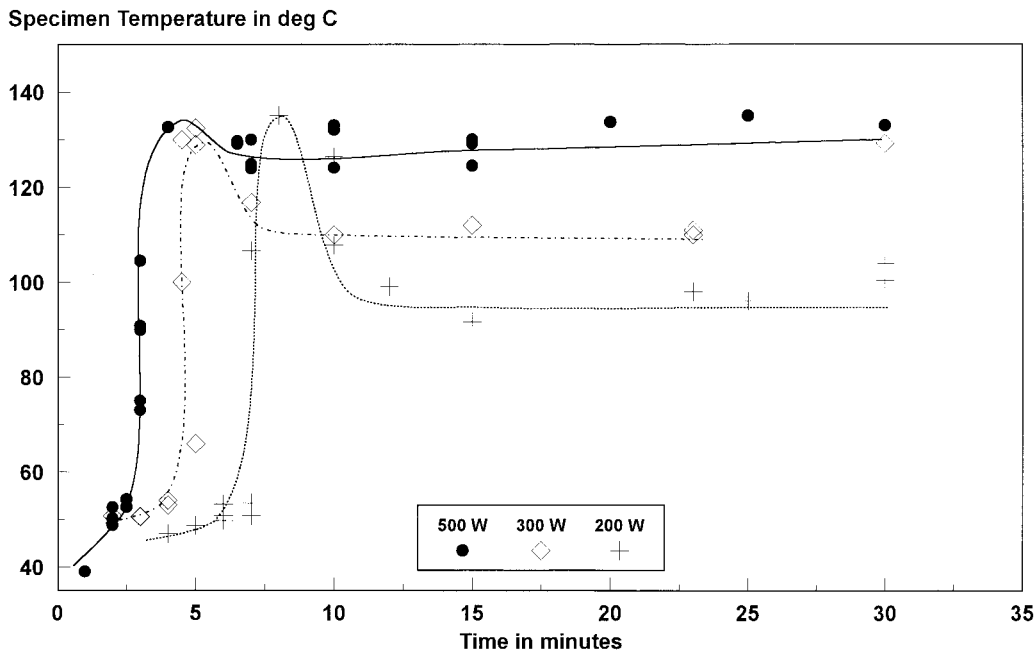


**Figure 3** Conversion and temperature profile with time for microwave polymerization of MA at 500 W.

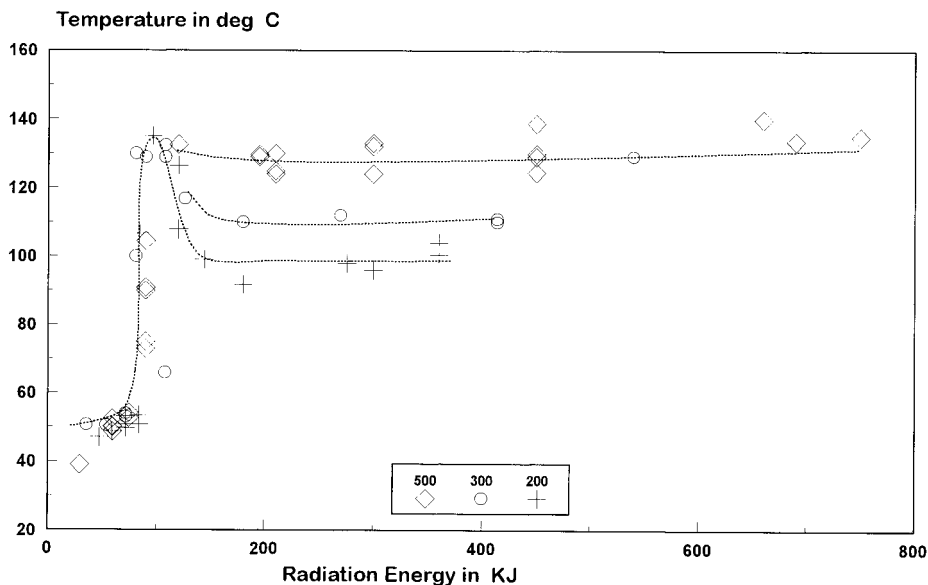
in °C,  $t$  is time in seconds,  $P_d$  is the power density absorbed by the material in ( $W/m^3$ ),  $C$  is the specific heat capacity of the material in  $J/Kg^{\circ}C$ , and  $\rho$  is the density of the material in  $Kg/m^3$ . The power density is determined by the variables given in eq. (2).

$$P_d = 0.556 \times 10^{-12} E^2 f \epsilon_r'' \quad (2)$$

where  $E$  is the electric field intensity,  $f$  is the frequency of the microwave, and  $\epsilon_r$  is the dielectric loss factor. From eqs. (1) and (2), the heating rate of microwave radiation at constant frequency,



**Figure 4** Comparison of specimen temperature for microwave polymerization of MA at 200, 300, and 500 W.



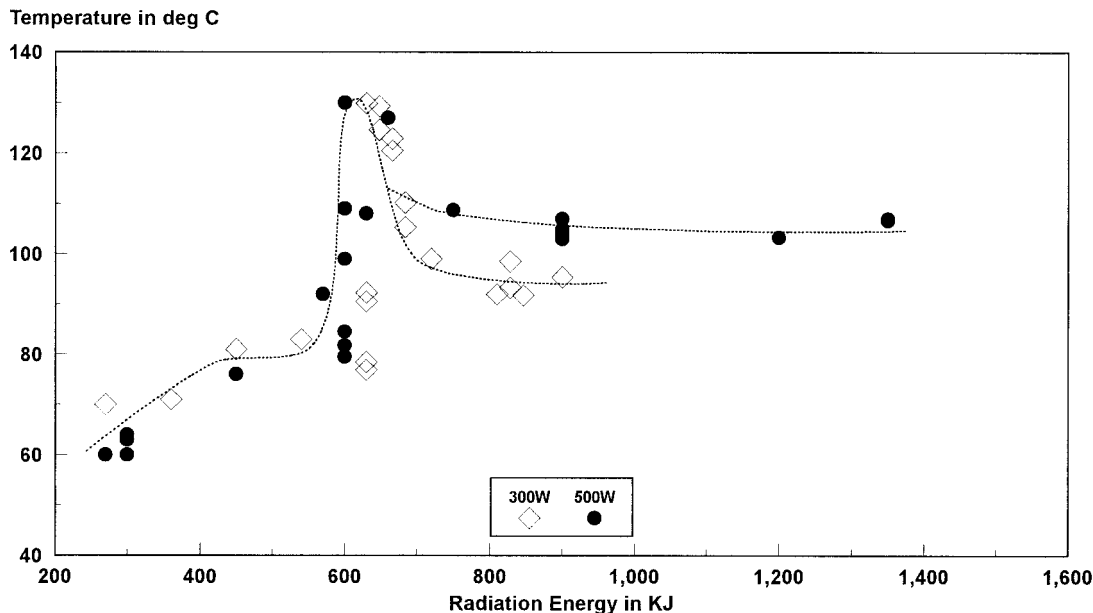
**Figure 5** Specimen temperature versus radiation energy for microwave polymerization of MA at 200, 300, and 500 W.

therefore, is determined by the dielectric loss factor, specific heat, density, and the applied electric field strength. Assuming that the dielectric loss factor, specific heat, and density of the irradiated material remain constant at different power settings, the heating rate is thus directly proportional to the applied field strength. Irradiating a material at 500 W microwave radiation compared to 200 W would result in an increased electric field strength applied to the material and, hence, an increased heating rate. Nevertheless, the specimen temperature need not be different at variable power settings. Rearranging eq. (2),

$$dT = P_a dt / C \rho \quad (3)$$

The product of power density and time is the energy of the radiation. It can be seen from eq. (3) that the energy of 500 W microwave radiation, applied to sample for 10 s would be  $5000 \text{ W/m}^3/\text{s}$ , and irradiating the sample at 200 W for 25 s would also be  $5000 \text{ W/m}^3/\text{s}$ . Accordingly, a plot of the specimen temperature against the microwave radiation energy at different power should show no difference in the specimen temperature, which was precisely observed as shown in Figure 5. A similar temperature profile for cure at variable power can be seen until the peak of the exothermic reaction. Along with the completion of the exothermic reaction, the specimen temperature declined. The decline in specimen temperature, how-

ever, was not similar for all three power settings, even though the mass of the sample was the same. The specimen temperature decreased in the following order:  $500 > 300 > 200 \text{ W}$ . A similar phenomenon was observed in the microwave polymerization of styrene at 300 and 500 W, which is shown in Figure 6.<sup>31</sup> The specimen temperature profile of the 300 and 500 W reaction was similar until the peak of the exothermic reaction, after which the specimen temperature decreased in the following order:  $500 > 300 \text{ W}$ . Tefal and Gourdene<sup>42</sup> also reported a similar behavior in the microwave polymerization of HEMA (2-hydroxyethyl methacrylate) at 96, 78, 63, 40, and 31 W. With the completion of the exothermic reaction, the specimen temperature declined in proportion to the applied power, even though the sample weight was the same in all the experiments:  $96 > 78 > 63 > 40 > 31 \text{ W}$ . The higher specimen temperature of the 96 W cure was attributed to the bubbles formed in the polymer matrix due to monomer boiling, which could have acted as a thermal insulator to the thermistor, thereby impairing the temperature measurement. In our experiments, however, the thermistor was inserted into the sample after completion of the reaction, and, therefore, impairment of the thermistor cannot be the reason for this unique behavior of the material under microwave radiation at variable power. At the end of the polymerization reaction, the specimen temperature is also affected by the



**Figure 6** Specimen temperature versus radiation energy for microwave polymerization of styrene at 300 and 500 W.<sup>31</sup>

rate of cooling in addition to the rate of heating. On continued irradiation, when the sample has cooled sufficiently, the specimen temperature now controlled by the rate of heating only should show a similar temperature profile at variable power, as observed during the initial period of polymerization. This, however, was not observed as evident in Figures 5 and 6. The specimen temperature of the 500 W reaction remained higher than the 300 W, even after prolonged irradiation of the system. Therefore the others are other factors operating in addition to the rate of cooling. From eq. (3), these other factors could be related to the specific heat, density, or dielectric loss of the material being different for the polymer formed at variable power settings. In our study on microwave polymerization of PMMA and PS,<sup>43</sup> the molecular weight of the polymers formed were found to decrease with increase in microwave power. A similar observation has been reported earlier.<sup>44</sup>

It implies from eq. (2) that when the energy of microwave radiation at 200, 300, and 500 W becomes similar with respect to time, the percentage conversion profile at various power settings should also be similar. This was indeed observed and is shown in Figure 7. It is noteworthy that even though the specimen temperature varied with different power settings at the end of the polymerization reaction, the limiting conversion remained unchanged for all the three power settings. The higher temperature of the 500 W reac-

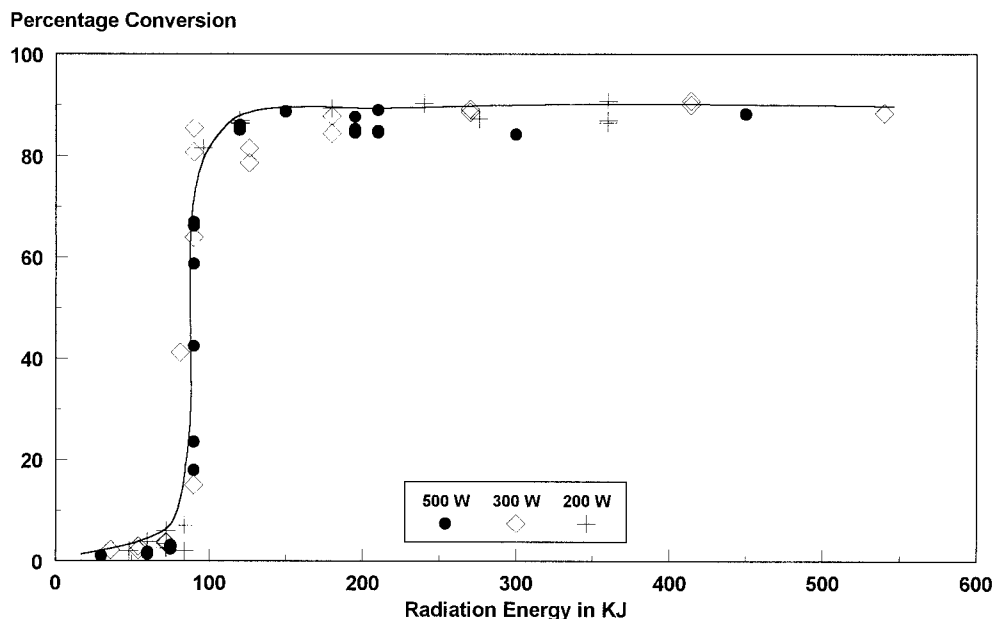
tion did not result in further increase in conversion beyond the observed limiting conversion.

### Thermal Polymerization of Styrene

The thermal polymerization of MA at the comparable temperature of  $52(\pm 1)^{\circ}\text{C}$  is shown in Figure 8. A plot of the specimen temperature just after thermal polymerization against the polymerization time is indicated by the dotted curve. A similar exothermic peak, as in microwave polymerization, was observed, with the peak temperature reached being lower than that observed in the microwave reaction of about  $115^{\circ}\text{C}$ . The maximum conversion in the thermal polymerization was  $83(\pm 1)\%$ , which was lower than the microwave polymerization of  $89(\pm 1)\%$  for all the three power settings. Reaction rate enhancement of the microwave polymerization compared to the thermal method under similar reaction conditions was calculated using the following method<sup>45</sup>:

$$\text{Rate enhancement} = \frac{\text{conventional reaction time}}{\text{microwave reaction time}} \quad (4)$$

where the conventional reaction time and microwave reaction time are for reactions taken to similar completion under the conditions employed. Rate enhancement for the reaction taken to about



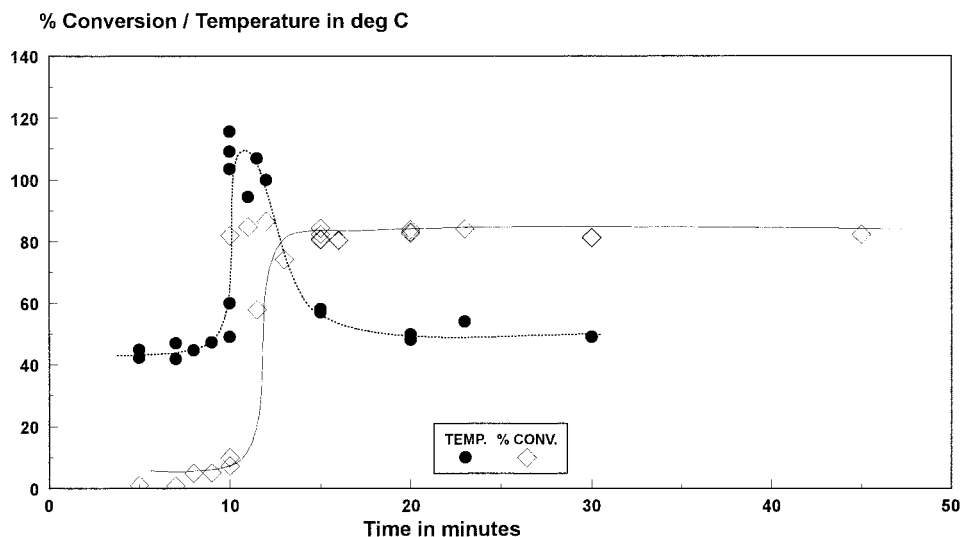
**Figure 7** Percentage conversion versus radiation energy for microwave polymerization of MA at 200, 300, and 500 W.

85% conversion, shown in Table II, was calculated from Figures 1–3 and 8.

#### Limiting Conversion in the Microwave Polymerization of MMA, MA, and Styrene

The limiting conversion of microwave polymerization (MA) at 200, 300, and 500 W was found to be  $89(\pm 1)\%$  (cf. Fig. 5). Unlike MA, the limiting conversion in the microwave polymerization of

MMA<sup>30</sup> and Styrene<sup>31</sup> was found to decrease with increase in microwave power, which is shown in Figures 9 and 10. (Continued polymerization, however, resulted in increased percentage conversion.) The only experimental difference in the microwave polymerization of MMA and styrene compared to that of MA was in the volume of the reaction vial. The microwave polymerization of MMA and styrene were carried out in 2 mL sample vials, while that of MA was in 4 mL sample



**Figure 8** Conversion and temperature profile with time for thermal polymerization of MA at  $52(\pm 1)^\circ\text{C}$ .



**Table II** Reaction Rate Enhancement of Microwave Polymerization of PMA Compared to the Thermal Method

Microwave Power (W)	Time at Limiting Conversion <sup>a</sup>	Reaction Rate Enhancement of PMA (%)
500	4	275
300	5	220
200	8	138

PMA, poly(methyl acrylate).

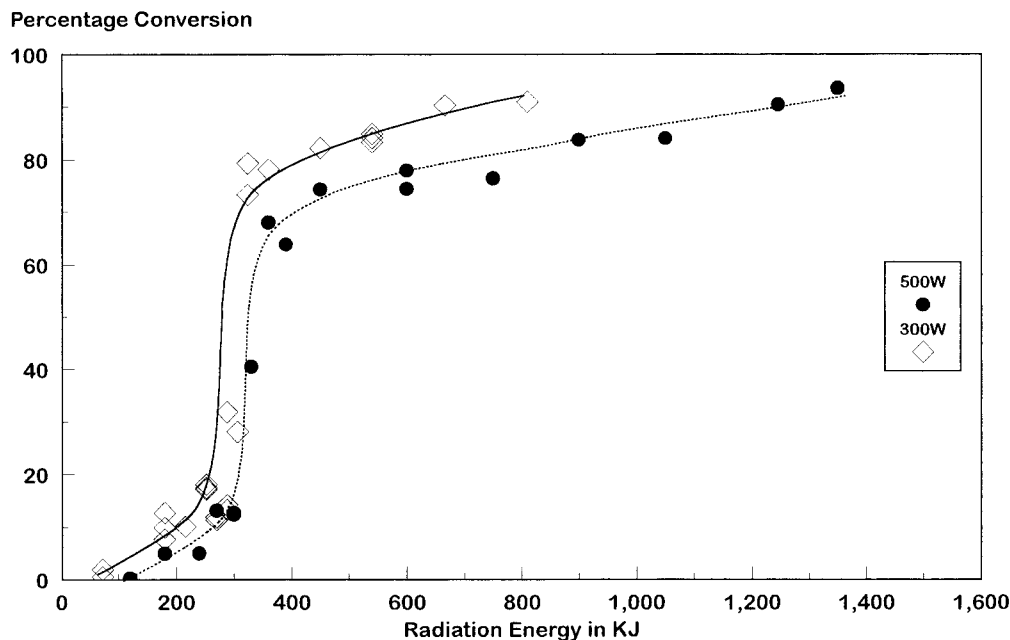
<sup>a</sup> Time at limiting conversion for the thermal method = 11 min.

vials. The decrease in limiting conversion with increase in microwave power observed in MMA and Styrene, therefore, may be related to volume–pressure effects of the sample vials. This was confirmed when the polymerization of MMA and styrene were carried out in 4 mL sample vials when the variation in limiting conversion with microwave power was removed. Thus, the results of PMMA and PS in the 2 mL vials indicate increasing pressure in the sample vials with increasing microwave power. Similar results of increase in pressure with microwave power has also been reported.<sup>45</sup> This phenomenon may be due to formation of hot spots during microwave irradiation, which increases with microwave power.

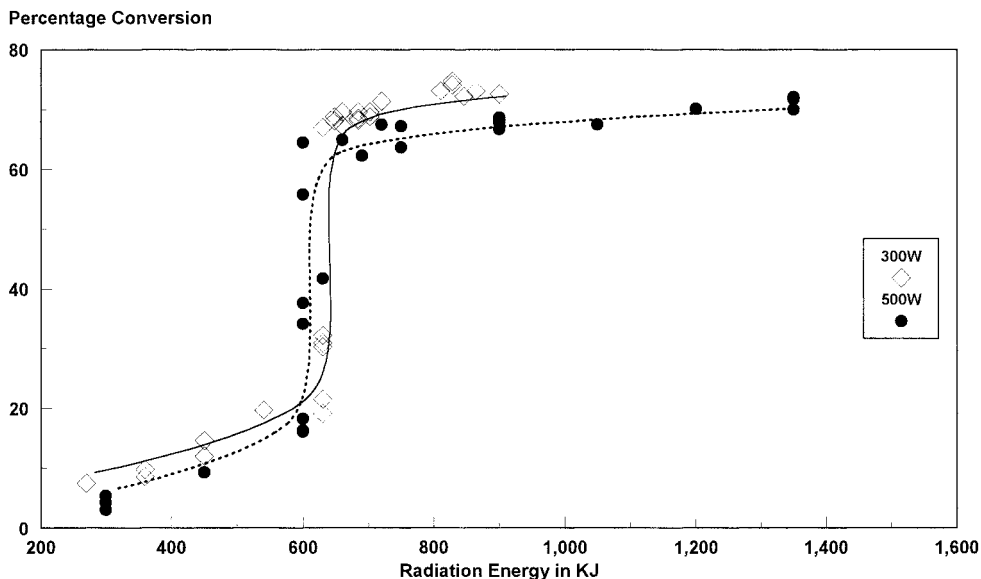
## CONCLUSION

The polymerization of MA with AIBN as initiator was carried out in bulk under microwave radiation at three different powers, namely, 200, 300, and 500 W. The temperature profile of the microwave irradiated sample was followed, and the temperature of the specimen at the onset of the exothermic reaction was selected for comparison of the microwave and thermal methods. The results indicate that a similar comparable temperature of about 52°C was observed for all the three power settings. The percentage conversion of the reaction was followed by FTIR spectroscopy. The reaction rate enhancement of microwave polymerization compared to the thermal method was found to be as follows: 500 W, 275%; 300 W, 220%; and 200 W, 138%. Even though the comparable temperature at variable power was the same, the reaction rate enhancement increased with increase in microwave power. This was because of the increased heating rate at higher microwave power. Comparison of microwave-activated reactions with the thermal method, therefore, must also specify the microwave power used.

The conversion profile of the microwave polymerization at 200, 300, and 500 W was shown to be similar when considered in terms of the energy of the radiation. The specimen temperature profile also was shown to be similar for the variable



**Figure 9** Limiting conversion for microwave polymerization of PMMA at 300 and 500 W.<sup>31</sup>



**Figure 10** Limiting conversion for microwave polymerization of PS at 300 and 500 W.<sup>31</sup>

microwave power during the polymerization stage but differed at the completion of the exothermic reaction.

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