

POLYMERIZATION OF METHYL METHACRYLATE BY HEAT-CATALYST AND GAMMA-IRRADIATION METHODS¹

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ABSTRACT

Methyl methacrylate (MMA) was bulk-polymerized with 0 to 4% crosslinker (ethylene glycol dimethacrylate, EGDM, and trimethylol propane trimethacrylate, TMPTM), initiated with 0.05 to 5% catalyst (Vazo) at 65–75 C or 0.1 to 1 Mrad/hr gamma radiation at 20 C. Heat-catalyzed MMA conversion to polymer vs. time was obtained directly from polymer mass, which indicated that about 90% conversion had occurred at the exothermic peak temperature. The time to the exothermic peak temperature was used to determine sample polymerization time. The over-all polymerization rate varied with the half-power of initiator concentration. An Arrhenius plot of the initiator-time data gave an activation energy of 18 kcal/mole. A log-log relationship was found between crosslinker concentration and polymerization time over the 65–75 C temperature and 0.1–0.4% initiator range. The crosslinkers were found equally efficient in reducing polymerization time. Peak exothermic temperature varied directly with time, irrespective of the initiator and crosslinker concentrations or bath temperature, except as they affected time. In the irradiation tests, the crosslinkers exhibited different data fits: log-log with EGDM and semilog for TMPTM. The time-dose rate equation for uncrosslinked MMA was analogous to that for heat-catalyzed polymerization. Molecular weight of uncrosslinked PMMA was determined as a function of temperature and catalyst concentration, and dose rate. Similar molecular weights were obtained for heat-catalyzed polymerization at 65 C and gamma irradiation at 20 C for numerically the same initiator concentration (%) and dose rate (Mrad/hr).

Since wood-plastic composites have become a commercial reality, more useful data have been needed on bulk polymerization of monomers. Little information is available on the *in situ* polymerization characteristics of wood-plastics (Beall et al. 1966). Information on commercialization of a wood-plastics irradiation process facility has recently been published (Witt and Morrissey 1972). Basic information was required to evaluate heat-catalyst and irradiation (gamma) bulk polymerization parameters and to establish relationships between the methods. Ultimately, the basic data will be used to examine the more complex wood-plastic system behavior under the non-steady-state conditions that occur in processing.

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MATERIALS AND METHODS

All materials were used as received from the manufacturer without further refinement. Table 1 shows the range of study variables associated with the materials. Heat catalyst tests were made over a temperature range of 65 to 75 C; irradiation was conducted at ambient temperature (20 C). Range of initiator concentration and dose rate was within nominal production limits.

Methyl methacrylate (MMA) was obtained from the manufacturer (DuPont) with an inhibitor concentration of 25 ppm BHT. Some of the physical properties of the two crosslinkers used (ethylene glycol dimethacrylate and trimethylol propane trimethacrylate) are compared with MMA in Table 2. The number of vinyl groups on a mass-percentage basis was nearly the same for all three monomers.

The azo initiator, Vazo (DuPont) decomposes to produce two free radicals and one

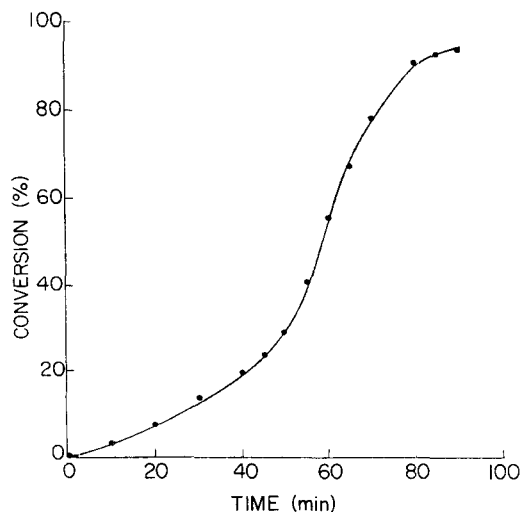


FIG. 1. Conversion of bulk-polymerized methyl methacrylate at 70 C with 0.2% Vazo.

nitrogen molecule. It is stable at room temperature (0.5% per month decomposition at 24 C) and decomposes by a first-order reaction. The single N_2 molecule evolved contrasts with molecular decomposition of benzoyl peroxide, which generates two CO_2 molecules. The half-life of Vazo at temperatures in the range of wood-plastic curing is about one-third of that for benzoyl peroxide.

In both portions of the study, the monomer was placed in 4-ml (1 dram) glass vials having polyethylene caps. Sample temperature measurements were made with 0.25-mm-diameter copper-constantan thermocouples. The thermocouple was inserted in a closed-end capillary tube and was aligned to center the junction in the monomer. The advantages of the capillary tube were: elimination of embedding of

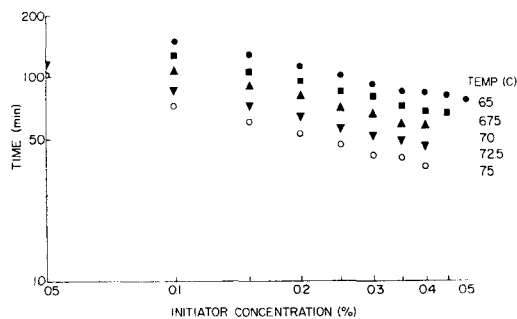


FIG. 2. Polymerization time for methyl methacrylate heat-catalyzed at 65 to 75 C with various Vazo concentrations.

the thermocouple in polymer, alignment of the thermocouple, and noncontamination of the monomer. Temperature data were collected on a 24-point recorder with compensated input terminals and a variable-zero, variable-span range with a system accuracy of ± 0.5 C. The adjustable e.m.f. limits provided the required sensitivity for the exothermic peaks.

The mass of monomer to be used in heat-catalyst tests was determined by a series of tests in which the exothermic peak area (temperature-time) was compared to the monomer mass. Calibration runs using 1.0 to 3.0 g MMA showed no significant difference in the 2.0- to 2.5-g range in either the time to the exothermic peak or the area-mass ratio; therefore, a 2.25-g mass (about 2.4 ml) was used. In the heat-catalyst tests, the vials were placed in a multiple (24) sample holder assembly in an oil bath controlled within ± 0.05 C of the set temperature.

The radiation polymerization was carried out in a hot-cell with circulating air at 20 C. Three planar sample holder assemblies were arranged between and on each side of two

TABLE 1. Materials and range of concentrations

Monomer	Methyl Methacrylate (MMA)	
Inhibitor	Butylated Hydroxytoluene (BHT)	25 ppm
Crosslinkers	Ethylene Glycol Dimethacrylate (EDMA)	1-4%
	Trimethylol Propane Trimethacrylate (TMPTM)	1-4%
Initiators	2,2'-azobis(isobutyronitrile) (Vazo ^a)	0.05-0.5%
	Co-60 gamma radiation	0.1-1.0 Mrad/hr

^a DuPont tradename.

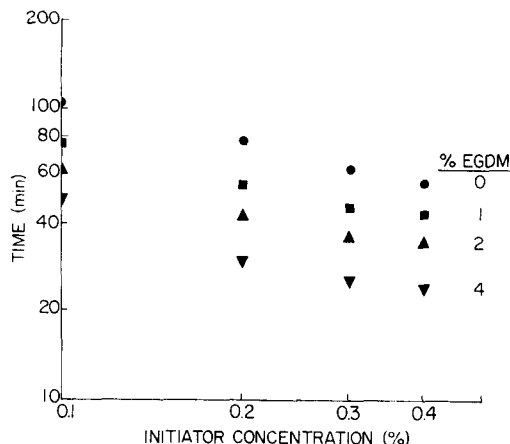


FIG. 3. Effect of concentration of ethylene glycol dimethacrylate (EGDM) and Vazo concentration on polymerization time of methyl methacrylate at 70 C.

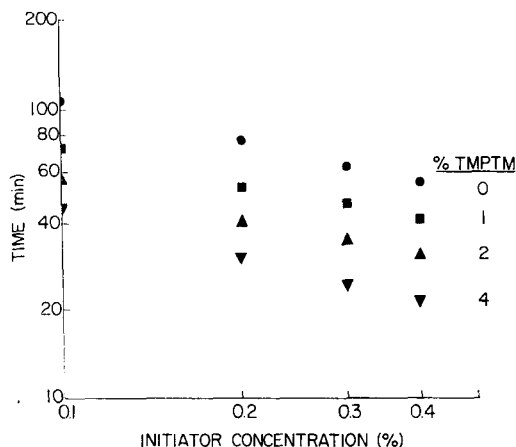


FIG. 4. Effect of concentration of trimethylol propane trimethacrylate (TMPTM) and Vazo concentration on polymerization time of methyl methacrylate at 70 C.

source plaques of Co-60 to obtain simultaneous irradiation at three dose rates. Each sample holder held 8 samples and 2 calibration vials. Nominal dose rates were determined by the position of the plaques and sample holders; actual dose rates were found after each run from the transmittance of Perspex samples in the calibration vials (Berry and Marshall 1969). Total activity of the Co-60 source was 35 kCi. The vials contained 4 g of monomer with a minimum of air space to reduce variations that could be caused by the presence of oxygen. A more discernible exotherm and temperature peak was also realized from the additional mass as compared with the heat-catalyst procedure.

RESULTS AND DISCUSSION

General heat-catalyst conversion

The variables related to monomer conversion without crosslinker were studied first. Data acquired from monomer conversion were later used as a reference for effects of additives.

Conversion vs. time

Figure 1 shows the mass conversion of MMA samples at 70 C and 0.2% Vazo. Conversion data were acquired by placing

identical samples in the bath for various time intervals, and cooling and drying the samples under vacuum at room temperature, followed by vacuum oven drying. This method appears reliable and simpler than the dilatometer method, where volumetric contraction is the variable measured. Direct mass determination also would be useful for monomers such as tertiary-butyl styrene, which has little volumetric contraction in polymerization. The inflection point at about 50 min coincides with an abrupt increase in viscosity (25–30% conversion). The curve is very similar to those obtained during thermal polymerization, which occurs at higher temperatures without a catalyst (Flory 1953). In this heat-catalyst system, under the conditions of Fig. 1, the first noticeable heat release was at about 65 min, at which 70% conversion had occurred. The exothermic peak in the system was at 78 min (about 90% conversion). Because of this, it appeared that the temperature peak was a reasonable reference point at which polymerization could be considered completed.

Vazo concentration

The effect of Vazo concentration and bath temperature on polymerization time is shown in Fig. 2. The time to the tempera-

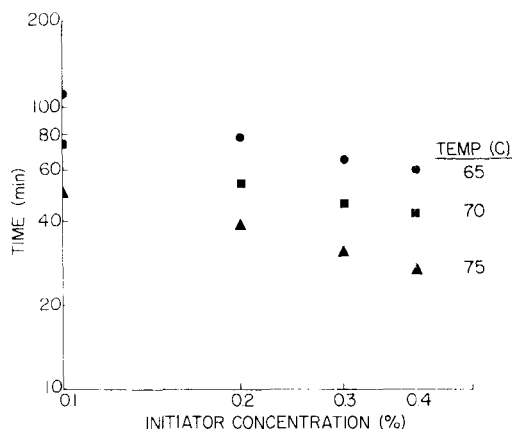


FIG. 5. Temperature effect on polymerization time of methyl methacrylate containing 1% EGDM or TMPTM as a function of Vazo concentration.

ture peak for each sample did not include the sample warm-up time. Warm-up time was determined experimentally by finding the time constant for the initial temperature increase (room to bath temperature) and assuming zero time after five time constants. Regression equations for the curves at each temperature were significant at the 99% level ($r^2 = 0.997$). The exponent of the equation for each curve, $t = AI^{-0.47}$, is a mean with $\pm 5\%$ variation. The overall rate of polymerization varies as the half-power of initiator concentration, $r = BI^{0.5}$, (Flory 1953); therefore, time to the temperature peak is inversely proportional to the polymerization rate ($t \propto 1/r$). High Vazo concentrations at the higher temperatures produced bubbles in the polymer. Bubble-free polymer was obtained below 0.35% Vazo at 70°C and 0.3% Vazo at 75°C. At 65°C, bubbles were not

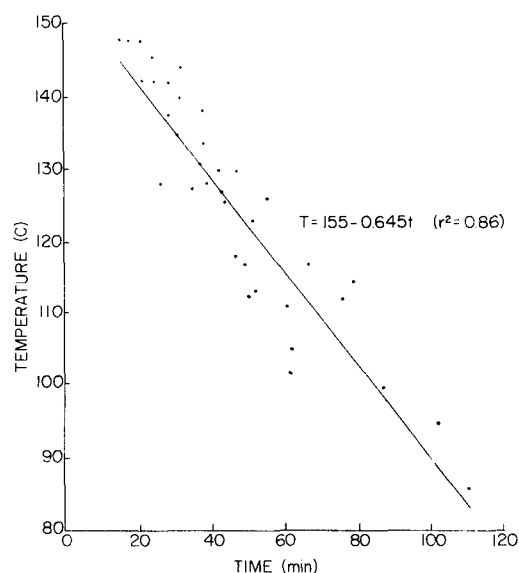


FIG. 6. Exothermic peak temperature of methyl methacrylate as a function of time to the peak for all combinations of crosslinker concentrations (1, 2, 4% EGDM), initiator concentrations (0.1–0.4% Vazo), and bath temperatures (65, 70, 75°C).

formed with less than 0.5% Vazo. An Arrhenius plot of the Fig. 2 data gave an activation energy of 18 ± 0.5 kcal/mole over 0.1 to 0.4% Vazo. This is in reasonable agreement with the theoretical value of 19.9 kcal/mole, based on idealized free-radical polymerization kinetics (Billmeyer 1970).

Crosslinker type and concentration

The heat-catalyst system provided sensitive, reproducible data for crosslinker effects on polymerization time. Figures 3, 4, and 5 represent a portion of the data collected from runs made at all combinations of temperature (65, 70, 75°C), Vazo con-

TABLE 2. Selected characteristics of methyl methacrylate monomer and crosslinkers^a

	MMA	EDMA	TMPTM
Color	clear	clear	clear, straw
Molecular wt.	100	198	338
B.P. (°C)	101 (760 torr)	260 (760 torr)	> 200 (1 torr)
Density (25°C)	0.94	1.05	1.065
Viscosity (25°C, cps)	0.84	3.4	35

^aSartomer Resins, Inc. Research Bulletin 2301.

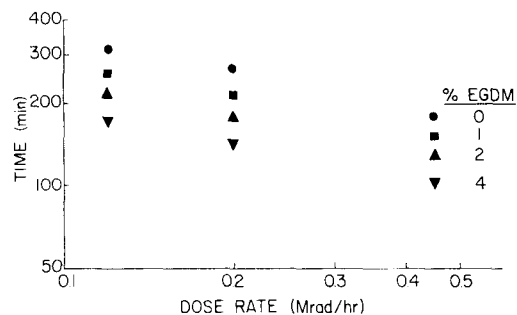


FIG. 7. Time to the exothermic peak of methyl methacrylate crosslinked with ethylene glycol dimethacrylate as affected by gamma dose rate.

centration (0.1–0.4%), and crosslinker concentration (1–4%). The compatibility of the crosslinkers with methyl methacrylate is obvious from the regularity of the data. For all data, the best fit was obtained from log-log plots. TMPTM (Fig. 4) differed from EGDM (Fig. 3) primarily in the points at high crosslinker and/or initiator concentrations. The data of Figs. 3 and 4 for 1 and 2% crosslinker concentration at all temperatures (65, 70, 75 C) and initiator concentrations (0.1–0.4%) could be fit with straight lines of slope 0.45. The variation was greater with EDMA ($\pm 10\%$) than TMPTM ($\pm 5\%$). The relative efficiency of crosslinkers in bulk polymerization was arbitrarily established as the time to the temperature peak for values of crosslinker concentration (1%), Vazo concentration

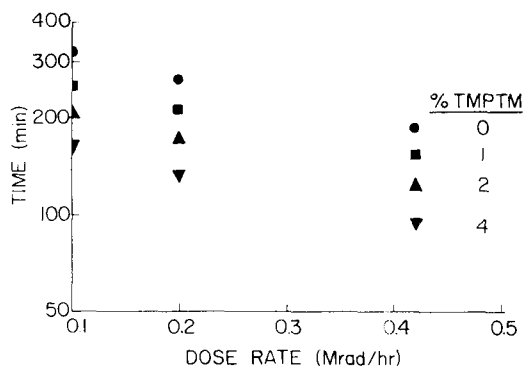


FIG. 8. Time to temperature peak of methyl methacrylate crosslinked with trimethylol propane trimethacrylate as affected by gamma dose rate.

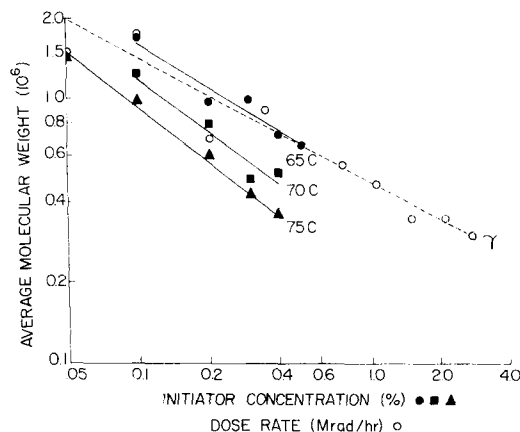


FIG. 9. Average molecular weight (inherent viscosity) for polymethyl methacrylate as affected by initiator concentration (Vazo) and temperature, or gamma dose rate.

(0.2%), and temperature (70 C), to be used as reference points in other related heat-catalyst tests. For EGDM/TMPTM, the time ratio was nearly unity (1.02). Figure 6 is a plot of peak temperatures recorded as affected by time to the exothermic peak. The slope of the curve was not appreciably affected by bath temperature, initiator concentration, or crosslinker concentration, except as it influenced the polymerization time. Such a curve may be used as a predicting equation for peak temperatures based on independent variable combinations.

In the irradiation series of tests, the same crosslinker concentrations were studied with dose rate as the independent variable. Figures 7 and 8 show the irradiation analogy of the heat-catalyst parameters. The form of the best fit of the data differed with EGDM and TMPTM. A general log-log relationship, $t = AD^{-0.41}$, was found for 1, 2, and 4% EGDM concentrations ($\pm 3\%$ slope variation). In contrast, TMPTM data had the best fit to a semilog plot, with the form of $t = Ae^{-1.7D}$ ($\pm 7\%$ slope variation) for 1, 2, and 4% concentrations. A log-log fit for uncrosslinked methyl methacrylate produced a curve, $t = AD^{-0.45}$, nearly analogous to that for the heat-catalyst behavior ($t = AI^{-0.47}$).

Molecular weight

Figure 9 shows molecular weight as a function of temperature, Vazo concentration, and dose rate. Molecular weight was determined from dilute inherent viscosity (2 mg MMA/ml benzene, 25 C) using conventional conversion techniques (Flory 1953). While nearly an inverse square root relationship (0.44) was obtained with the radiation series, an inverse $\frac{2}{3}$ -power ($\pm 10\%$) was found for the heat-catalyst tests. Of particular interest is the analogy of dose rate and Vazo concentration (65 C) in producing an equivalent molecular weight.

Comparison of heat-catalyst vs. irradiation polymerization times for methyl methacrylate required a convenient reference. The reference point was selected on the basis of molecular weights, 65 C and

0.2% Vazo for the heat-catalyst time, and 20 C and 0.2 Mrad/hr for irradiation time. A ratio of 2.35 (irradiation time/heat time) at these points indicates the relative time required to produce polymer with the same molecular weight.

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