

## *Effects of Dissolved Monomers in the Methyl Methacrylate- $\alpha$ -Methyl Styrene Copolymer System*

### Introduction

Numerous writers have pointed out the effect of dissolved monomers or plasticizers on the properties of thermoplastic polymers.<sup>1-7</sup> Their studies generally show an improvement in processibility but a reduction in mechanical, thermal, and chemical resistance properties with increasing monomer content.

The studies reported herein concerned the effect of methyl methacrylate (MMA) and  $\alpha$ -methyl styrene ( $\alpha$ -MS) monomers at 0.6 to 2.0 wt.-% in the polymer produced in the free-radical bulk polymerization of a 3:1 blend of these components, respectively. The ratio of MMA to  $\alpha$ -MS monomers investigated ( $\approx 1:1$ ) was in the range normally re-

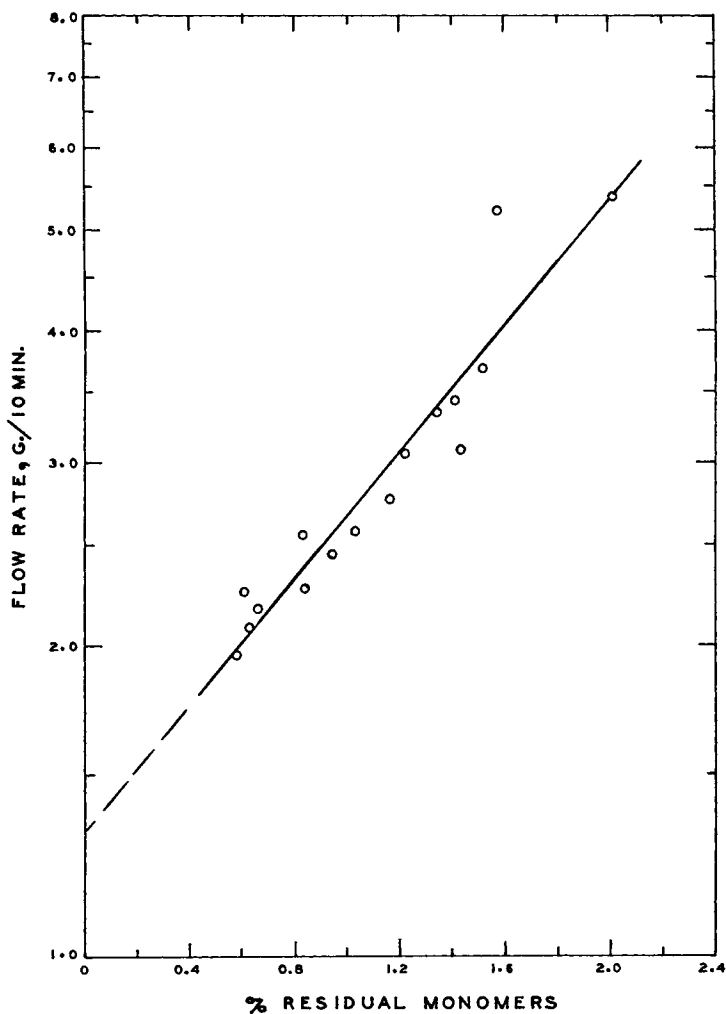


Fig. 1. Effect of residual monomers on flow rate of MMA- $\alpha$ -MS copolymer.

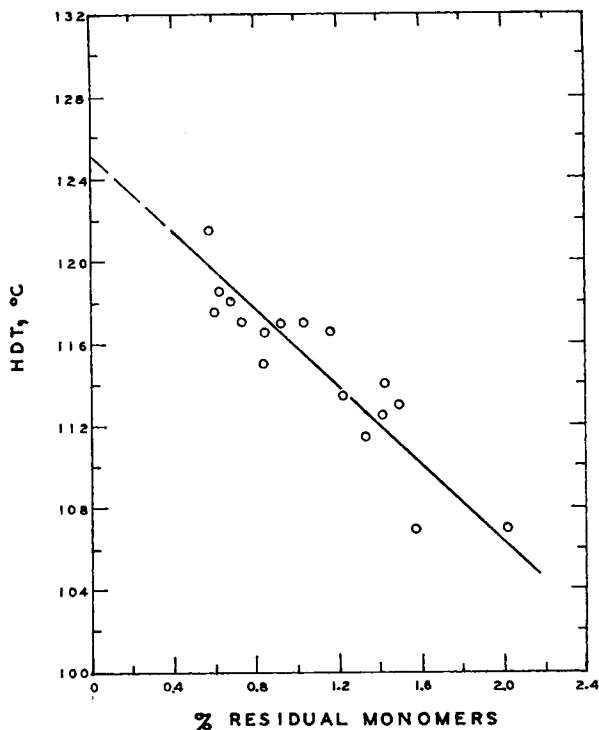


Fig. 2. Effect of residual monomers on heat-deflection temperature of MMA- $\alpha$ -MS copolymer.

maining after copolymerization to about 94 wt.-% conversion. The properties investigated included flow rate, heat-deflection temperature, tensile and flexural strength, and development of yellowness during heat aging and exposure to ultraviolet rays plus heat.

#### Experimental

The copolymer was prepared by free-radical bulk polymerization of a 3:1 weight ratio of methyl methacrylate to  $\alpha$ -methyl styrene.<sup>8</sup> The polymerization proceeded to 94% conversion, and the bulk of residual monomers was removed during vacuum extrusion of the molten polymer. The strands were then pelletized.

Residual monomers were determined in the pelletized copolymer by gas-liquid chromatography. A 10 g. polymer sample was dissolved in 30 ml. of  $\text{CH}_2\text{Cl}_2$ , and 1 ml. of a 5% butyl benzene solution was added as an internal standard. The copolymer was then precipitated by addition of MeOH to form 100 ml. of the mixture. The supernatant was then analyzed by passing the mixture through a 15 ft. by  $\frac{1}{8}$  in. Apiezon on a Chromasorb W column. MMA was eluted at 50°C., and the instrument was programmed to increase in temperature at 15°C./min. up to 150°C., at which temperature  $\alpha$ -MS and butyl benzene were eluted. A flame ionization detector was used for measuring the components. The areas of the monomer peaks were compared with that of butyl benzene and were corrected for relative sensitivity according to prepared standards. The values obtained for MMA and  $\alpha$ -MS were combined and, based on the original polymer weight, gave the per cent residual monomers.

The flow rate was measured in grams extruded from a 0.0825 in. diam. orifice at 230°C. under a pressure of 100 psi in a melt indexer of the type described in ASTM D 1238.

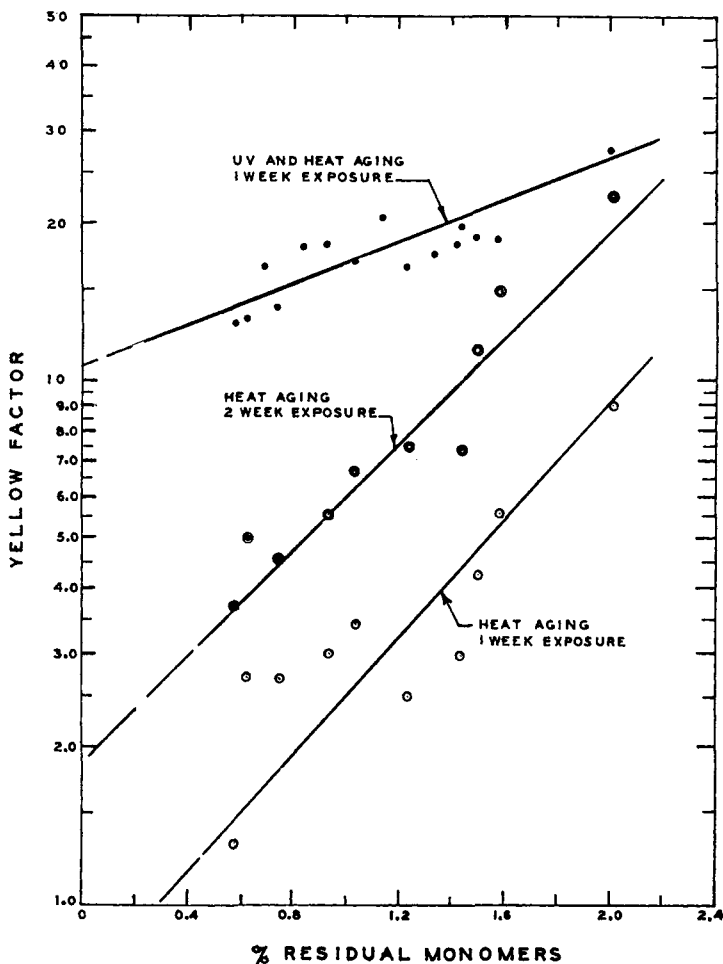


Fig. 3. Effect of residual monomers on yellowing of MMA- $\alpha$ -MS copolymer under thermal and ultraviolet exposure.

Heat-deflection temperature (HDT) bars 5 in. by  $\frac{1}{2}$  in. by  $\frac{1}{2}$  in. were compression-molded, and measurements were made according to ASTM D 648.

Heat-aging specimens 3 in. by  $\frac{1}{2}$  in. by  $\frac{1}{8}$  in. were made by compression molding. Heat aging at 1 and 2 weeks at 107.5°C. was conducted in a Blue M black-heat oven with an air atmosphere. The initial and the exposed specimens were analyzed with a Beckman DK-1 Recording Spectrophotometer at 420, 560, and 680  $m\mu$  wavelengths. The yellow factor was calculated as follows:

$$YF = [(T_{420} - T_{420}') - (T_{680} - T_{680}')]/T_{560}$$

where  $T$  is transmission of unexposed specimen at indicated wavelength, and  $T'$  is transmission of exposed specimen at indicated wavelength. The specimens for heat and ultraviolet exposure were identical with those prepared for heat-aging tests. They were exposed in an E-1 test apparatus developed by the General Electric Company. It was composed of a 400-w. E-1 ultraviolet bulb mounted vertically within a 12-in. diam., internally blackened chimney. The samples were mounted on rods projecting upward from the periphery of an 8-in. diam. turntable operating at 16 rpm. The centerline of the

specimens was equal in height to the filament of the bulb, and the specimens were approximately 2 in. horizontally from the glass of the bulb at the closest point. The heat in the chimney was provided by the lamp itself, and the temperature at the specimen location was controlled at  $75 \pm 3^\circ\text{C}$ . by regulating the escape of heat through the top of the chimney. The atmosphere was air. The yellow factor was measured after 1 wk. of exposure.

### Discussion

As shown in Figure 1, the polymer flow rate in the extrusion plastometer increases significantly with increasing monomer content in accordance with the equation

$$\ln \text{FR} = 0.701(\%M) + 0.278$$

where FR is the flow rate and %M is the weight per cent of monomers. By assuming that the flow rate is inversely proportional to the melt viscosity the data can be accurately described by the Flory equation  $\log \eta = A + B(w_2)^{1/2}$ , where  $A$  and  $B$  are constants, and  $w_2$  is the weight fraction of the polymer.

Thus, the flow rate increases from 1.3, at which the monomer-free polymer is difficult to process in injection-molding, to 2.3, at which the polymer, now 0.8% monomer, is of a relatively workable grade.

The adverse effect of dissolved monomers on the HDT is shown in Figure 2. It can be seen that the HDT decreases by  $9.5^\circ\text{C}$ . per per cent monomer content from an extrapolated value of  $125^\circ\text{C}$ . for a monomer-free polymer.

There was no significant effect of monomer concentration on the tensile and flexural properties in the monomer-content region of 0.6–2.0 wt.-%.

As shown in Figure 3, yellowing of the MMA- $\alpha$ -MS polymeric system increases significantly with increasing monomer content under heat at  $107^\circ\text{C}$ . or ultraviolet exposure plus heat at  $75^\circ\text{C}$ . in the presence of air. The intercepts of the curves on the ordinate indicate that the polymer is more resistant to thermal discoloration than to ultraviolet irradiation at the energy levels involved. On the other hand, the steeper slopes suggest that the monomers are more discolored by the heat than by the ultraviolet energy. No attempt was made to separate the effects of oxidation from those of thermal and ultraviolet discoloration.

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