

# ***0558 Residual Monomer in PMMA: Kinetics and Thermodynamics***

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Objectives: To determine the dependence of methyl methacrylate (MMA) monomer concentration [M] on time (t/h) and temperature (T/K) during polymerization in poly(methyl methacrylate) (PMMA) and thus to identify optimum processing conditions according to the thermodynamics and kinetics of the system as it is known that free-radical polymerizations are equilibria, thus:  $M \rightleftharpoons PMMA$ .

Methods: 100 mg PMMA + 6  $\mu$ L MMA was sealed in a 2 mL glass tube, treated at chosen (t,T), and quenched at  $-20\pm C$ . The tube contents were then dissolved in 5 mL dichloromethane, and 2  $\mu$ L of the solution taken for gas chromatographic analysis by direct injection (previously validated), and the value of [M] calculated. The response surface equation was constructed by inspection of the slope in the various domains and integration (Mathematica). The overall minimum was then found by differentiation.

Results: The data were found to fit the equation below, where  $z = [1000/T + f.\log(t) - d]/a$ , in which  $a = -0.28$ ,  $b = 0.051$ ,  $c = 11.18$ ,  $d = 2.74$ ,  $e = 1.33$ ,  $f = -0.21$ . The minimum value for [M] was obtained at about 24 h at  $100\pm C$ , shorter time being inadequate for reaction; higher temperature is dominated by the shift in equilibrium.

Conclusions: PMMA with no residual monomer is not attainable as the polymer is in equilibrium with a T-dependent value of [M]. The usual denture base processing conditions do not approach optimum with respect to [M].

$$\log[M] = e \left\{ b + \left[ \left( e^{-z^2} / \sqrt{\pi} \right) + z + (z - c) \operatorname{Erf}(z) \right] / c \right\} / 2$$

[Seq #77 - Chemistry IV](#)

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[Back to the Dental Materials: V - Polymer Materials-Chemistry Program](#)  
[Back to the IADR/AADR/CADR 82nd General Session \(March 10-13, 2004\)](#)