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 <--> PMMA.

Methods: 100 mg PMMA + 6 µL MMA was sealed in a 2 mL glass tube, treated at chosen (t,T), and quenched at -20≡C. The tube contents were then dissolved in 5 mL dichloromethane, and 2 µL 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≡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 equilbrium with a T-dependent value of [M]. The usual denture base processing conditions do not approach optimum with respect to [M].

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

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