

## CORRECTION OF TELOMER CHAIN TRANSFER CONSTANT DATA BY DIGITAL COMPUTER INTEGRATION

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A recent paper (1) from this laboratory reported data which indicated that a reactivity minimum occurred in the free radical telomerization of methyl acrylate with ethanethiol. This was especially interesting since it seemed to parallel results found in similar systems involving bromotrichloromethane as the chain transfer agent (2). The data in question indicated that the chain transfer constant for the three-unit radical ( $C_3$ ) was substantially higher than for the two-unit radical ( $C_2$ ) and also for long chain polymer radicals ( $C_\infty$ ). These data consisted of ratios of successive telomers formed at low conversion determined at various mercaptan-to-monomer ratios by gas chromatography. By substitution in equation 1 the first three chain transfer constants were calculated according to the method of Scott and Wang (3). The left hand side of

$$\frac{d[B-M_n-A]}{d[B-M_{n+1}-A]} = C_n[AB]/[M] + \dots C_n/C_{n+1} \quad (1)$$

where  $[AB]$  and  $[M]$  are the monomer and thiol concentrations, respectively, and  $C_n$  and  $C_{n+1}$  refer to  $C_1$  and  $C_2$ , or  $C_2$  and  $C_3$ .

equation 1 is approximated by the measured telomer ratios; but since this is a differential equation, its accuracy is limited by the extent to which the mercaptan-to-monomer ratio remains constant during the course of the reaction. The change in monomer concentration was measured and maintained less than ten percent. The change in mercaptan concentration should always be less than this, but it was not measured owing to its high volatility.

Since the results of the study were based on the plausible but unchecked assumption that variations in the mercaptan-to-monomer ratios were too small to substantially effect the resulting chain transfer constants, it is desirable to determine these changes from the data already available if possible.

This paper reports calculation of the change in this ratio for all experimental points based on the assumption that the constants calculated in reference 1 are valid and that all constants above  $C_3$  are equal to  $C_\infty$ .

### METHOD OF CALCULATION

Differential equations relating the ratio of consumption of monomer to mercaptan can be derived in several ways. For example

equation 2, used in these calculations, can be derived from a general expression reported by Walling (equation 21, reference 4). (This allows for variation of chain transfer constants through  $C_i$ ; however  $C_i$  was set equal to  $C_\infty$  in all calculations reported below.) Relationships between mercaptan and monomer concentrations at varying conversions were determined using a simple step-by-step numerical integration procedure based on the relationship

$$Y_2 = Y_1 - \Delta X dY/dX$$

where  $X = [AB]$  and  $Y = [M]$  in equation 2.

The operations were programed in IBM Fortran II for the 1620 computer, to recalculate  $Y$  in very small steps between a fixed value  $Y_0$  and zero.

Figure 1 shows that typical calculations of  $Y$  converge asymptotically to a constant value as the number of steps is increased. Figure 2 shows that resulting curves are nearly linear. Apparently no more complex numerical integration procedure (such as Heun's or Milne's method) is required to obtain sufficiently accurate results.

All experimental mercaptan-to-monomer ratios listed in reference 1 were corrected according to the percent monomer consumed. The resulting points were then used to recalculate the chain transfer constants.

Equation (2)

$$\frac{d[M]}{d[AB]} = 1 + \frac{1 + \frac{[M]}{[AB]} \cdot \frac{1}{C_\infty} + \left[ \frac{[AB]}{[M]} C_4 + 1 \right] \left[ \left( \frac{[AB]}{[M]} C_3 + 1 \right) \left( \frac{[AB]}{[M]} C_2 + 2 \right) + 1 \right]}{\left( \frac{[AB]}{[M]} C_1 + 1 \right) \left( \frac{[AB]}{[M]} C_2 + 1 \right) \left( \frac{[AB]}{[M]} C_3 + 1 \right) \left( \frac{[AB]}{[M]} C_4 + 1 \right)}$$

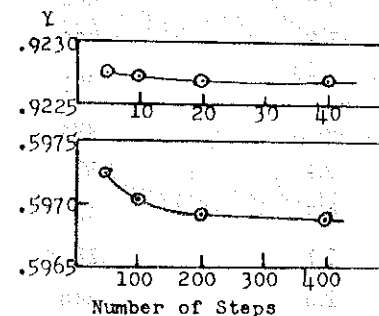


Figure 1

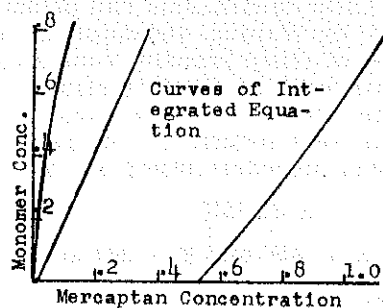


Figure 2

## RESULTS

Table I lists the original experimental ratios, the extreme values calculated for the measured percentages of monomer consumption and the arithmetic means of these values. Since the curves are so nearly linear these means should correspond to the effective concentrations to apply in equation 1. The resulting slopes, intercepts, and chain transfer constants calculated by the method of least squares are listed in Table II together with the corresponding standard deviations. It will be noted that only minor differences appear.

TABLE I

Original Value	% Conversion	Calculated Final Value	Mean
.202	5.4	.1987	.200
.457	7.4	.451	.454
.712	3.3	.720	.716
.854	5.0	.871	.862
.960	10.0	.994	.977
1.22	9.4	1.33	1.265
.130	4.7	.1272	.129
.189	5.1	.1858	.1874
.444	2.8	.445	.444
.655	8.6	.672	.663
.842	9.8	.876	.859

TABLE II

	Least Squares Value		Standard Deviation	
	Original	Corrected	Original	Corrected
C <sub>1</sub> Slope	0.78	0.74	.011	.012
Intercept	.434	.449	.011	.012
C <sub>2</sub> (from Intercept)	1.79	1.65		
C <sub>3</sub> Slope	1.61	1.58	.11	.11
Intercept	.34	.35	.096	.092
C <sub>4</sub> (from Intercept)	5 (4.72)	5 (4.54)		

## REFERENCES

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3. (a) J. C. Robb and E. Senogles, *Trans. Faraday Soc.*, 58, 708 (1962); (b) W. J. Kirkham and J. C. Robb, *ibid.*, 57, 1757 (1961); (c) J. C. Robb and D. Vofsi, *ibid.*, 55, 558 (1959); (d) W. I. Bengough and R. A. M. Thompson, *ibid.*, 57, 1928 (1961); (e) 56, 407 (1960).
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