Note on the Continuous Measurement of Polymerization Rates with a Recording Dilatometer

In the dilatometric measurements of polymerization rates, a knowledge of the density of polymer solutions over the entire concentration range is necessary to determine the polymerization rates over the entire range of conversion. Rubens and Skochdopole[1] developed a dilatometer capable of measuring the volume change during polymerization over the entire conversion range. They also derived expressions relating the weight per cent polymer to the dilatometric data carried out to complete conversion based on the additivity of monomer and polymer volumes as well as the additivity of monomer and polymer densities. It is the purpose of this paper to derive more general expressions valid over the complete conversion range relating the weight per cent polymer to the dilatometric data based on both additivity of volumes and the additivity of densities.

To compare the results obtained from the different expressions based on both additivity of volumes and the additivity of densities, a hypothetical experiment was made on the polymerization of styrene at 80°C. in a glass tube of 1 cm.² cross-sectional area based on 100 g. of initial styrene monomer. The values of polymer and monomer densities used for these calculations were taken from the paper by Rubens and Skochdopole.[1] They are $d_1 = 0.8502$ g./cc. and $d_2 = 1.0356$ g./cc. (subscripts 1 and 2 refer to monomer and polymer, respectively).

The specific volume, V_{12}, of a polymerizing solution at any time t may be expressed in terms of the partial specific volumes of monomer $\bar{V}_1$ and polymer $\bar{V}_2$ by the equation

$$V_{12(t)} = w_{1(t)} \bar{V}_{1(t)} + w_{2(t)} \bar{V}_{2(t)} \tag{1}$$

where w_2 represents the weight fraction of polymer. If we define F as the per cent conversion of monomer to polymer at time f given by

$$F = (\bar{V}_{1(f)} - V_{12(f)})/(\bar{V}_{1(f)} - \bar{V}_{2(f)}) \tag{2}$$

and C_F as the correction factor for F when the polymerization rate is to be determined at any time t other than at time f as is given by

$$C_F = (\bar{V}_{1(f)} - \bar{V}_{2(f)})/(\bar{V}_{1(t)} - \bar{V}_{2(t)}) \tag{3}$$

then, after substitution of eqs. (2) and (3), eq. (1) can be rearranged to yield

$$w_{2(t)} = \left(\frac{\bar{V}_{1(t)} - V_{12(t)}}{\bar{V}_{1(t)} - \bar{V}_{2(t)}}\right) = \left(\frac{\bar{V}_{1(t)} - V_{12(t)}}{\bar{V}_{1(f)} - V_{12(f)}}\right) F C_F \tag{4}$$

For an ideal thermodynamic polymer solution (no volume change on mixing), C_F becomes unity and the partial specific volumes are equal to the pure component volumes V, and eqs. (1), (2), and (4) reduce to

$$V_{12(t)} = w_{1(t)}V_1 + w_{2(t)}V_2 \tag{5}$$

$$w_{2(t)} = [(R_0 - R_t)/(R_0 - R_f)]F \tag{6}$$

$$F = (R_0 - R_f)/(R_0 - R_{100}) \tag{7}$$

where R_0 is the initial height of styrene monomer in the tube, R_t is the height of polymer solution at time t, R_f is the final height of polymer solution at time f, and R_{100} is the height of polymer solution (or pure polymer) at 100% conversion. Equation (6) is the same equation obtained by Rubens and Skochdopole[1] based on the additivity of pure volumes.

Rubens and Skochdopole[1] also proposed an empirical linear density relationship for the case of polystyrene in ethylbenzene.

$$d_{12(t)} = w'_{1(t)}d_1 + w'_{2(t)}d_2 \tag{8}$$

where d represents the density and w' represents the weight fraction calculated assuming the empirical additivity of densities of pure components. The above equation can be written as follows, after substitution of $1/V$ for d:

$$w'_{2(t)} = \frac{(d_{12(t)} - d_1)(d_{12(f)} - d_1)}{(d_{12(f)} - d_1)(d_2 - d_1)} = \left(\frac{V_1 - V_{12(t)}}{V_1 - V_{12(f)}}\right)\left(\frac{V_{12(f)}}{V_{12(t)}}\right) F' \tag{9}$$

where F' is the per cent conversion of monomer to polymer at time f based on the empirical linear density relationship and is given by

$$F' = (d_{12(f)} - d_1)/(d_2 - d_1) \tag{10}$$

Substituting eq. (8) into eq. (9) and realizing that $w'_{2(f)} = F'$ by definition, we obtain

$$w'_{2(t)} = \left(\frac{R_0 - R_t}{R_0 - R_f}\right) \frac{[(1 - w'_{2(t)})d_1 + w'_{2(t)}d_2]F'}{[(1 - F')d_1 + F'd_2]} \tag{11}$$

The above equation can be solved for $w'_{2(t)}$ to yield

$$w'_{2(t)} = \frac{d_1}{\left(\dfrac{R_0 - R_f}{R_0 - R_t}\right)\left(\dfrac{d_1}{F'} + d_2 - d_1\right) - (d_2 - d_1)} \tag{12}$$

Equation (12) is compared with the following expression derived by Rubens and Skochdopole for the dilatometric data carried out to complete conversion

$$\frac{w'_{2(t)}}{F'} = \frac{V_1 V_2}{\left[(V_1 - V_2)\dfrac{(R_0 - R_t)}{(R_0 - R_f)}(V_2 - V_1) + V_1\right]} - \frac{V_2}{V_1 - V_2} \tag{13}$$

Table I compares the results of the previously described hypothetical experiment as calculated by eqs. (6) and (12). These results are compared with the values obtained from eq. (13) based on the additivity of densities observed by Rubens and Skochdopole.

TABLE I
Comparison of Calculated Per Cent Conversion of Styrene at 80°C. by Additivity of Volumes and Additivity of Densities

R_t, cm.	$0 < F \leq 1$ eq. (6)	$0 < F \leq 1$ eq. (12)	$F = 1$ eq. (13)	$F = 0.977$ eq. (13)	$F = 0.4$ eq. (13)	eq. (6)–eq. (12) / eq. (6) $\times$ 100, %
113.41	20.00	17.03	17.03	16.97	15.93	14.85
111.30	30.00	26.03	26.03	25.95	24.98	13.23
109.20	40.00	35.37	35.37	35.28	34.89	11.58
107.09	50.00	45.08	45.08	44.98	45.78	9.84
104.99	60.00	55.19	55.19	55.09	57.83	8.02
102.88	70.00	65.70	65.70	65.61	71.29	6.14
100.77	80.00	76.66	76.66	76.59	86.16	4.18
98.67	90.00	88.08	88.08	88.04	102.97	2.13

Equations (6) and (12) give the same conversion at a given volume contraction for all values of F. This means that one could carry out the polymerization up to 20–30% conversion and calculate the polymerization rates over the entire conversion range, if the expression for the density of polymer solution is accurately known. On the other hand, eq. (13) gives different conversions at a given volume contraction for different values of F. Equations (12) and (13) are identical when F is unity, but the difference

between these two equations becomes larger as F decreases. When F is less than unity, eq. (13) gives erroneous results over the entire conversion range. However, the deviation is quite small as long as F is close to unity. The difference between the additivity of volumes and the additivity of densities is shown in the last column of Table I. In conclusion, for experiments carried out to low conversions, eq. (12) of this paper should be used instead of eq. (13) [eq. (5) in reference 1].

Reference

1. L. C. Rubens and R. E. Skochdopole, *J. Appl. Polymer Sci.*, **9**, 1487 (1965).

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