

## Conversion Factors in Dilatometric Data of Polymerization Reactions

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### Synopsis

Various factors in the conversion of dilatometric data to the extent of polymerization have been considered. These factors are volume additivity, density additivity, difference between the thermal coefficients of monomer and polymer, molecular weight, and degree of crosslinkage. Equations relating the dilatometric readings to the extent of polymerization have been derived. These equations can be used for reactions where the polymerization may be stopped short of complete polymerization. They can also be used for polymerization where the initial portion of the reaction is difficult to record.

### INTRODUCTION

The dilatometric method is frequently used to follow the course of polymerization reaction. The volume shrinkage which occurs during polymerization is the result of the reduction of intermolecular distance between monomer units as they enter the polymer chains. While the operation is simple, it is necessary to calibrate the dilatometer and eliminate any factors that interfere with data recordings.<sup>1-4</sup> The major problem in the interpretation of dilatometric data is relating the observed volume shrinkage to the extent of polymerization.<sup>4-7</sup> In most cases, ideal thermodynamic solution behavior is assumed, and the additivity of monomer and polymer volumes to form the volume of polymer solution is the basic calculation. It has been shown that the monomer and polymer volumes may not be additive in some systems.<sup>2,6,8</sup> An empirical relationship assuming additivity of densities of monomer and polymer has also been proposed.<sup>2,7</sup> Nichols and Flowers have shown that the fractional shrinkage of some vinyl and alkyl monomers can be accurately calculated from the volume of revolution of the monomer molecule about its major axis.<sup>9</sup> It has been postulated that the polymerization of a vinyl monomer involves the exchange of a double bond and a van der Waals bond for two covalent bonds.<sup>10</sup> This latter postulate was used by Loshaek and Fox, who concluded that molar interactions of the various methacrylates are similar, i.e., 22-23 cc/mole at 30°C.<sup>11</sup> These aspects will be further discussed in this paper.

The thermal expansion coefficients of monomers are usually larger than those of their polymers. Therefore, larger molar volume thermal shrinkage

TABLE I  
Dilatometric Data and Degree of Completion of the Reaction in Time (From Ref. 4).  
Reactions of Hexamethylene Diisocyanate with Poly(diallylene Glycol Adipate)

Initial data	Time, min	$\Delta V \times 10^3$ , ml	$\frac{\Delta V^a}{10.46}$	$\partial = \frac{C_\tau^b}{1.98}$	$C_\tau^c$
Initial volume = 3.57 ml $\Delta V = 2.05$	5	12.30	0.117	0.12	1.74
	10	18.85	0.180	0.18	1.62
	15	24.20	0.231	0.23	1.52
	20	27.30	0.261	0.26	1.46
Contraction = 2.93% ( $\partial = 1$ )	25	30.80	0.294	0.30	1.39
	30	34.60	0.331	0.33	1.31
Initial concentrations = 1.98 g/equiv/l.	35	37.30	0.357	0.36	1.27
	40	41.60	0.398	0.40	1.19
	45	45.10	0.431	0.43	1.12
	50	47.80	0.457	0.46	1.07
	55	49.80	0.476	0.48	1.03
	60	51.20	0.498	0.49	1.01
	70	53.30	0.510	0.51	0.96
	80	55.80	0.533	0.54	0.92
	90	57.40	0.549	0.55	0.89
	110	59.20	0.566	0.57	0.85
	130	61.10	0.584	0.59	0.85
	155	63.20	0.604	0.61	0.78

<sup>a</sup>  $(\Delta V \text{ at time } t)/(\Delta V \text{ for complete polymerization}) = \text{conversion based on volume additivity.}$

<sup>b</sup> Conversion calculated from bromination.

<sup>c</sup> Concentration of diisocyanate at various time (g/equiv/l.) obtained by bromination.

than calculated would be observed.<sup>12</sup> A conversion factor will be included to account for this fact.

According to the observations on fractionated polystyrene, the specific volume of a polymer varies with its molecular weight.<sup>12,13</sup> Since the specific volume of the polymer is an important factor in the calculation of dilatometric data, the effect of molecular weight should also be considered in the calculation. The effect of degree of crosslinking upon the volume contraction will also be discussed.

### RELATING THE OBSERVED VOLUME SHRINKAGE TO THE EXTENT OF POLYMERIZATION

In polymerizations, the percentage change in volume is proportional to the numbers of monomers entering the polymer chains and inversely proportional to the monomer molecular volume. Therefore, it should be possible to measure volume changes and equate these values to per cent conversion of monomer to polymer.

There are few data on the densities of polymer solutions to provide conversion factors for dilatometric data. In most cases, ideal thermodynamic solution behavior is assumed and the volumes of monomer and polymer are treated as additive:

$$V_{ps} = [(wt\text{-}\% p)V_p + (wt\text{-}\% m)V_m]/100. \quad (1)$$

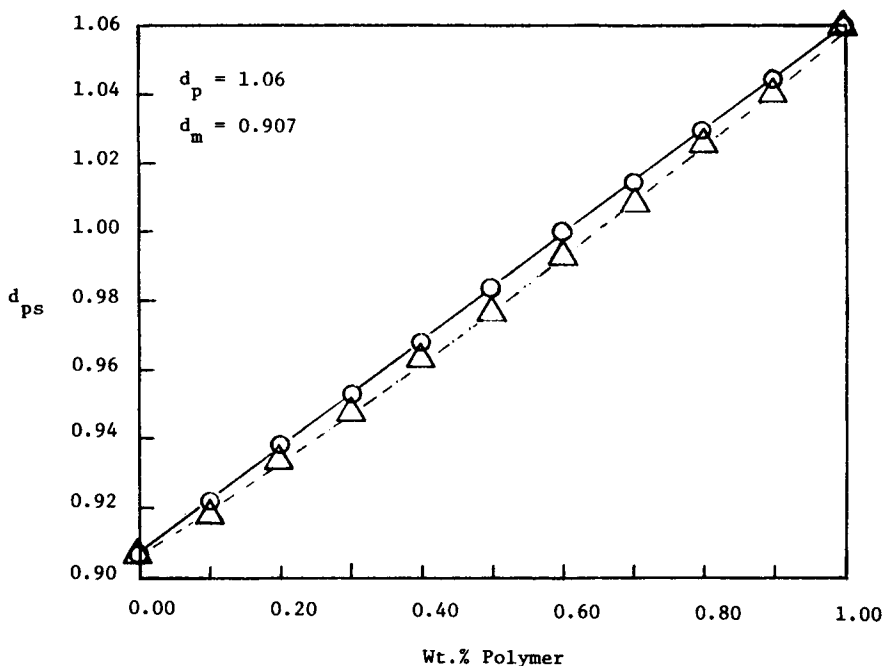


Fig. 1. Density of polymer solution: (O) density additivity; ( $\Delta$ ) volume additivity.

This equation can be written in terms of densities:

$$d_{ps} = 100 / [(wt\% p/d_p) + (wt\% m/d_m)] \quad (2)$$

where  $ps$  = monomer-polymer solution,  $p$  = polymer,  $m$  = monomer,  $V$  = specific volume, and  $d$  = density.

Some kinetic data on a polyurethane system are taken from the literature and shown in Table I.<sup>4</sup> The extent of conversion calculated by assuming volume additivity is given in column 4. The extent of reaction determined by bromination is given in column 5. The agreement between values on both columns is quite good. Therefore, the volume additivity method is adequate in this case.

For the polystyrene system, Rubens found that densities instead of volumes were additive.<sup>2</sup> Thus, the equation for the density of the polymer solution is given in eq. (3):

$$d_{ps} = [(wt\% p)d_p + (wt\% m)d_m]/100. \quad (3)$$

In order to demonstrate the difference between density and volume additive assumptions, eqs. (2) and (3) are used to calculate the density of a hypothetical system having  $d_p = 1.06$  and  $d_m = 0.907$  (similar to a polystyrene and styrene system). The two corresponding series of values are plotted in Figure 1 for comparison. The density of the polymer solution increases faster if it is linear with respect to its component densities. For a given density value of the polymer solution, the two assumptions give results that differ by more than 10% in calculating the corresponding conversion.

Equations to calculate per cent conversion from dilatometric data assuming density and volume additivities are:

*Density additivity*

$$\text{wt.-% polymer} = \frac{100}{d_p - d_m} \left[ \frac{w_{m,I}}{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)} - d_m \right] \quad (4)$$

*Volume additivity*

$$\text{wt.-% polymer} = \frac{100 \pi r^2(R_0 - R_t)}{w_{m,I} \left( \frac{1}{d_m} - \frac{1}{d_p} \right)} \quad (5)$$

where  $w_{m,I}$  = initial weight of monomer,  $d_m$  = density of monomer,  $d_p$  = density of polymer,  $r$  = radius of the fine capillary tube of the dilatometer,  $R_0$  = initial height of the mercury in the dilatometer, and  $R_t$  = height of mercury at time  $t$ .

Derivatives of eqs. (4) and (5) are given in Appendixes A and B. Equations (4) and (5) are similar to the equations of Rubens, except for the expressions of initial and final dilatometric readings.

According to the work of Loshaek and Fox on linear vinyl esters,<sup>11</sup> the volume shrinkage resulting from polymerization is 23 ml/mole double bond at 30°C. The equation for volume shrinkage is

$$\% \text{ shrinkage} = \frac{23 \text{ ml}}{\text{molar volume}} \quad (6)$$

but

$$d_m = \frac{(\text{molecular weight})_m}{(\text{molar volume})_m} \quad (7)$$

or

$$(\text{molar volume})_m = \frac{(\text{molecular weight})_m}{d_m} \quad (8)$$

Substituting eq. (8) into eq. (6),

$$\% \text{ shrinkage} = \frac{23 \text{ ml}}{(\text{molecular weight})_m} \times d_m \quad (9)$$

Density values of the corresponding monomeric and polymeric materials of a number of compounds are taken from the literature. Their volume shrinkages for complete polymerization calculated according to eq. (9) are listed in Table II. The shrinkage values calculated from the volume additivity equation are also shown in Table II. Most of the corresponding values calculated from the volume additivity agree closely with those calculated from eq. (9).

The density and volume additivities and the 23 ml/mole method all seemed to be good approximation methods for certain systems. For precise results, it is desirable to make independent density measurements of the monomer and polymer solution at various concentrations.<sup>2,5,6</sup>

TABLE II  
Calculated Shrinkage Values for Vinyl and Allyl Monomers  
During Complete Conversion to Polymer

Monomer	Molecular weight $M$ , g/mole	$d_m$ , <sup>a</sup> g/ml	$d_p$ , <sup>a</sup> g/ml	$1 - \frac{d_m}{d_p}$ , <sup>b</sup> % shrink	$\frac{d_m}{M} \times 23$ , <sup>c</sup> % shrink
Vinyl chloride	62.50	0.919	1.406	0.346	0.338
Acrylonitrile	53.06	0.797	1.17	0.319	0.345
Vinylidene bromide	185.86	2.178	3.053	0.287	0.269
Vinylidene dichloride	96.96	1.22	1.71	0.287	0.290
Vinyl bromide	106.96	1.512	2.075	0.271	0.324
Methacrylonitrile	67.09	0.800	1.10	0.273	0.274
Methyl methacrylate	100.12	0.940	1.19	0.210	0.216
Vinyl acetate	86.09	0.932	1.19	0.217	0.248
Diallyl succinate	198.22	1.056	1.30	0.188	0.122
Ethyl methacrylate	114.15	0.911	1.11	0.179	0.184
Diallyl maleate	196.20	1.077	1.30	0.172	0.126
<i>n</i> -Propyl methacrylate	128.17	0.902	1.06	0.149	0.161
Styrene	104.14	0.907	1.10	0.176	0.200
<i>n</i> -Butyl methacrylate	142.20	0.889	1.05	0.153	0.143
Isobutyl methacrylate	142.20	0.889	1.02	0.128	0.143
Diallyl phthalate	246.26	1.12	1.27	0.118	0.104
Diallyl tetrachlorophthalate	339.02	1.36	1.49	0.087	0.092
Chlorostyrene	138.60	1.0950	1.2478	0.122	0.182

<sup>a</sup> From ref. 9.

<sup>b</sup>  $d = w/V$ ;  $V_p/V_m = d_m/d_p$ ;  $1 - V_p/V_m = 1 - d_m/d_p$ ;  $(V_m - V_p)/V_m \times 100\% = \%$  shrinkage  $= 1 - d_m/d_p$ .

<sup>c</sup> Assumes shrinkage = 23 ml/(mole double bond) =  $(23 \times d_m)/M$ .

### DIFFERENT PERCENT CONVERSION FOR A GIVEN SHRINKAGE AT DIFFERENT TEMPERATURE

Since the thermal coefficients of expansion of monomers are usually larger than those of their corresponding polymers, the volume shrinkage with polymerization increases with temperature. The data of Rubens on *o*-chlorostyrene and styrene illustrated this point very well. They are reproduced in Figure 2.

In order to account for the difference in thermal coefficients of the monomer and polymer, the densities of monomer and polymer at a given temperature are expressed in two functions of densities at a reference temperature ( $T_1$ ) and their thermal coefficients of expansions:

$$d_{m,T_2} = \frac{d_{m,T_1}}{1 + \alpha_m(T_2 - T_1)} \quad (10)$$

$$d_{p,T_2} = \frac{d_{p,T_1}}{1 + \alpha_p(T_2 - T_1)} \quad (11)$$

where  $d_{m,T_2}$  = density of monomer at  $T_2$ ,  $d_{p,T_2}$  = density of polymer at  $T_2$ ,  $d_{m,T_1}$  = density of monomer at  $T_1$ ,  $d_{p,T_1}$  = density of polymer at  $T_1$ ,  $T_1$  = reference temperature,  $T_2$  = temperature of polymerization reaction,  $\alpha_m$  = volume thermal coefficients of monomer, and  $\alpha_p$  = volume thermal coefficients of polymer.

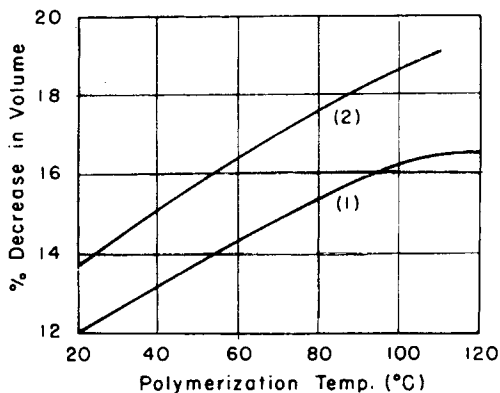


Fig. 2. Volume changes during polymerization: (1) *o*-chlorostyrene; (2) styrene (from ref. 14).

Derivatives of eqs. (10) and (11) are given in Appendix C. Equations (10) and (11) can be substituted into eqs. (4) and (5) to correct for the temperature effect on densities of monomer and polymer.

The thermal coefficients of expansion of monomer and polymer ( $\partial_m$  and  $\partial_p$ ) should be determined experimentally. It is also desirable to make measurements of monomer-polymer solution densities as a function of concentration.

Another point of interest is the treatment of polymer density when the temperature of polymerization is below its glass transition temperature ( $T_g$ ). The  $T_g$  of polystyrene is around 100°C, and the polymerization temperature is usually lower. The value of  $\partial_p$  is  $0.6 \times 10^{-3}$  g/cc/°C above  $T_g$  and  $0.27 \times 10^{-3}$  g/cc/°C below it.<sup>5</sup> Cooper and Smith<sup>5</sup> pointed out that in the styrene-polystyrene solution, polystyrene behaves more like a liquid than a solid. Therefore, its density in solution would be nearer to that obtained by extrapolation of the  $d_p$  versus  $T$  curves for the polymer above  $T_g$  to the low polymerization temperature.

### CORRECTION FACTORS DUE TO INFLUENCE OF MOLECULAR WEIGHT AND DEGREE OF CROSSLINKING ON THE SPECIFIC VOLUME

According to the observations on fractionated polystyrene, the specific volume of a polymer varies with its molecular weight.<sup>12,13</sup> In addition, a decrease in specific volume accompanies the introduction of crosslinks into a polymer. The molecular weight influence on specific volume can be calculated by an equation in the paper of Fox and Loshaek<sup>13</sup>:

$$V(P) = V_0(\infty) + \partial_\infty T + \frac{(m + m_l)(\Delta\partial T + \Delta V_0)}{M} \quad (12)$$

where  $V(P)$  = specific volume for a polymer of degree of polymerization  $P$ ,  $V_0(\infty)$  = value of the limiting specific volume (for a chain of infinite length) extrapolated to  $T = 0^\circ\text{K}$ ,  $m$  = weight of an  $x$  unit,  $m_l$  = combined weight of the two chain ends,  $\Delta\partial = \partial_l - \partial_\infty$  (where  $\partial_l$  = thermal coefficient of monomer and  $\partial_\infty$  = thermal coefficient for the infinite chain length),  $\Delta V_0 = V_0(l) -$

$V_0(\infty)$  (where  $V_0(l)$  = value of specific volume for the monomer extrapolated to  $T = 0^\circ\text{K}$ ), and  $M$  = molecular weight of the polymer chain =  $mP + m_l$ .

Similarly, another equation from the same origin can be used to correct for the effect of crosslinkage:

$$V(\rho, M) = V_0(\infty) + \partial_\infty T + \frac{m(\Delta\partial T + \Delta V_0)}{M} - [\Delta\partial_x T + \Delta V_0(x)]M_x\rho \quad (13)$$

where  $\rho$  = crosslinks per gram of final polymer,  $\Delta\partial_x = \partial_x - \partial_\infty$  (where  $\partial_x = dV(x)/dT$ ),  $\Delta V_0(x) = V_0(x) + V_0(\infty)$  (where  $V_0(x)$  = specific volume of an  $x$  unit extrapolated to  $T = 0^\circ\text{K}$ ), and  $M_x$  = weight of two atoms eliminated in crosslinkage.

## CONCLUSIONS

Various factors in the conversion of dilatometric data to the extent of polymerization have been considered. Equations relating the dilatometric readings to the extent of polymerization have been derived. These equations can be used for reactions where the polymerization may be stopped short of complete polymerization. They can also be used for polymerization where the initial portion of the reaction is difficult to record.

It has been shown that the difference between the thermal coefficients of monomer and polymer can be corrected in the dilatometric data. The effect of molecular weight and degree of crosslinkage can also be accounted for.

## Appendix A

### Degree of Conversion Calculated From Additivity of Densities of Monomer and Polymer

According to Rubens' empirical equation of density additivity,<sup>2</sup> the density of the partially polymerized polymer solution can be calculated as<sup>2</sup>

$$d_{ps} = [(\text{wt.}\% p)d_p + (\text{wt.}\% m)d_m]/100 \quad (14)$$

where  $d$  = density,  $m$  = monomer,  $p$  = polymer,  $ps$  = monomer-polymer solution, and

$$d_{ps} = \frac{\text{wt of polymer solution}}{\text{volume of polymer solution}} = \frac{w_{m,I}}{V_0 - \pi r^2(R_0 - R_t)} \quad (15)$$

where  $w_{m,I}$  = initial weight of monomer introduced (total weight of material),  $V_0$  = initial volume of the material =  $w_{m,I}/d_m$ ,  $R_0$  = initial height of mercury in the dilatometer with cylindrical tube,  $R_t$  = height of mercury at time point  $t$ , and  $r$  = radius of the fine cylindrical tube of the dilatometer.

Rewrite eq. (15) as follows:

$$d_{ps} = \frac{w_{m,I}}{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)} \quad (16)$$

Substituting eq. (16) into eq. (14) yields

$$\frac{w_{m,I}}{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)} = \frac{[(\text{wt.}\% p)d_p + (\text{wt.}\% m)d_m]}{100} \quad (17)$$

Let

$$x = \text{wt-}\% p \quad (18)$$

then

$$\text{wt-}\% m = 100 - x. \quad (19)$$

Substituting eqs. (18) and (19) into eq. (17) yields

$$\frac{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)}{100} = \frac{[x d_p + (100 - x)d_m]}{100}$$

Rearrange,

$$\frac{100 w_{m,I}}{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)} = x(d_p - d_m) + 100d_m$$

or

$$x = \frac{100}{d_p - d_m} \left[ \frac{w_{m,I}}{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)} - d_m \right] \quad (20)$$

= wt-% polymer.

The advantage of using eq. (20) is that no other absolute method is required to determine the extent of conversion at the termination of the experiment. The value of  $R_0$  can be calculated from the density and initial amount of monomer. Therefore, eq. (20) can also be used for rate measurement where the initial part of the reaction cannot be recorded due to experimental difficulty (e.g., very fast initial reaction).

## Appendix B

### Degree of Conversion Calculated from Additivity of Volumes of Monomer and Polymer

If one assumes that the volumes of monomer and polymer are additive, the specific volume of the polymer solution is

$$V_{ps} = \frac{[(\text{wt-}\% p)V_p + (\text{wt-}\% m)V_m]}{100} \quad (21)$$

where  $V_{ps}$  = specific volume of polymer solution,  $V_p$  = specific volume of polymer, and  $V_m$  = specific volume of monomer.

Since  $1/d_{ps} = V_{ps}$ ,  $1/d_p = V_p$ , and  $1/d_m = V_m$ , eq. (21) can be rewritten as follows:

$$d_{ps} = \frac{100}{[(\text{wt-}\% p/d_p) + (\text{wt-}\% m)/d_m]} \quad (22)$$

Substituting eqs. (15), (18), and (19) into eq. (22),

$$\frac{\frac{w_{m,I}}{d_m} - \pi r^2(R_0 - R_t)}{100} = \frac{x}{d_p} + \frac{100 - x}{d_m} \quad (23)$$

Rearrange eq. (23):

$$x = \frac{100 \pi r^2(R_0 - R_t)}{w_{m,I} \left( \frac{1}{d_m} - \frac{1}{d_p} \right)} \quad (24)$$

= wt-% polymer.



## Appendix C

## Different Percent Conversion for a Given Shrinkage at Different Temperature

The density variations of monomer and polymer materials over a range of temperatures are quite different. This factor has to be accounted for in dilatometric measurements. The volume of a material can be expressed as a function of its thermal coefficient of expansion and temperature as follows:

$$V_{T_2} = V_{T_1} [1 + \alpha(T_2 - T_1)] \quad (25)$$

where  $V_{T_2}$  = volume at temperature  $T_2$ ,  $V_{T_1}$  = volume at temperature  $T_1$ , and  $\alpha$  = volume thermal coefficient of expansion.

Since the weight of the material stays constant,

$$\frac{dT_1}{dT_2} = \frac{V_{T_2}}{V_{T_1}} \quad (26)$$

Substituting eq. (26) into eq. (25),

$$dT_2 = \frac{dT_1 \cdot V_{T_1}}{V_{T_2}} = \frac{dT_1 \cdot V_{T_1}}{V_{T_1}[1 + \alpha(T_2 - T_1)]} = \frac{dT_1}{1 + \alpha(T_2 - T_1)} \quad (27)$$

where  $d$  = density.

Equation (27) can be written for the corresponding monomer and polymer materials of a compound:

$$d_{m,T_2} = \frac{d_{m,T_1}}{1 + \alpha_m(T_2 - T_1)} \quad (28)$$

$$d_{p,T_2} = \frac{d_{p,T_1}}{1 + \alpha_p(T_2 - T_1)} \quad (29)$$

where  $\alpha_m$  = volume coefficient of expansion of monomer and  $\alpha_p$  = volume coefficient of expansion of polymer.

Equations (28) and (29) can be substituted into eqs. (20) and (24) to correct for the temperature effect on dilatometric data.

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