

## Continuous Measurement of Polymerization Rates over the Entire Conversion Range with a Recording Dilatometer

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### Synopsis

A new type dilatometer has been described which will automatically record the volume changes which occur during the entire course of polymerization reactions. Experiments have shown that the weight per cent polymer in a monomer solution is more accurately described as a function of additive densities of monomer and polymer than of additive volumes of monomer and polymer. The operation of the dilatometer, the relation of the observed volume changes to monomer conversion to polymer, and the possible errors involved in these type measurements have been discussed. The apparatus has been used to obtain rate curves for the polymerization of both linear and crosslinked vinyl monomer compositions over the entire course of polymerization, despite the early formation of a firm crosslinked gel structure in the latter case.

### Introduction

Accurate polymerization rate data during the entire course of the reaction is of considerable importance in polymer science. From a practical standpoint, this information may (a) provide a most sensitive analysis to detect certain trace impurities in a monomer and (b) aid in selection of an optimum polymerization schedule. Data on the rates of polymerization have also provided a basis for development of the classical concepts for the reaction mechanisms of vinyl polymerization. A number of methods have been utilized for measuring the rate of conversion of monomer to polymer. The idea of using a dilatometer to measure the contraction which occurs when monomers are polymerized is not new. Over thirty years ago Starkweather and Taylor<sup>1</sup> determined the polymerization rate of vinyl acetate in this manner. It was difficult to follow the entire polymerization reaction with the early dilatometers for the following reasons.

(1) The monomer was in a rigid container attached to a capillary. As the viscosity increased or gelation occurred, the meniscus in the capillary would no longer drop as the volume of resin decreased. Bubbles and voids occurred in the resin at high conversion resulting in erratic results.

(2) The shape of the polymerization vessel did not permit rapid enough heat transfer to the surrounding medium to dissipate the exotherm of highly reactive systems, and isothermal conditions were therefore not maintained.

Shultz and Harborth<sup>2</sup> provided a solution to these problems by floating the monomer on top of mercury and holding it in a thin sheet in a glass tube. This method yielded good results but required cleaning of glass tubes prior to each experiment. The technique was also difficult to apply with viscous monomer systems.

### Apparatus

The development of a new type of dilatometer described here resulted from a desire to obtain rate data over the complete range of conversion of highly reactive, viscous monomer systems typified by unsaturated polyester-styrene mixtures. These materials form weak, crosslinked gels during the early stages of polymerization. After formation of the gel the reaction may be completed in a very short time (5-10 min.), resulting in a rapid rate of heat evolution.

Two important considerations were obvious in the design of a dilatometer for this purpose: (1) maximum contact of monomer with a high heat transfer medium was necessary to insure isothermal polymerization; (2) the reaction vessel should contract with the resin to prevent bubble and void formation. Both requirements were met by putting the monomer into a flexible film bag inside a rigid cell which supported the bag in the form of a thin sheet. The cell was then filled with a high thermal conductivity fluid which surrounded the film bag of monomer and extended up into an attached capillary to allow measurements of volume changes in the cell

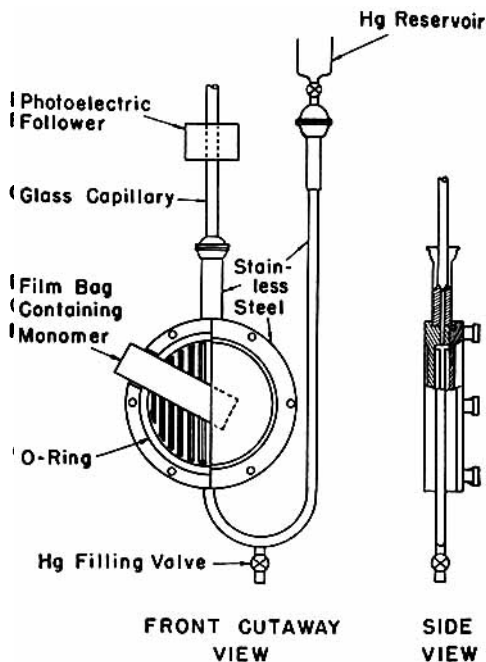


Fig. 1. Recording dilatometer.

contents. By enclosing the monomer sample in a disposable bag, problems of cleaning the dilatometer between runs were eliminated.

The choice of a film for the monomer container is of critical importance. It must possess the following properties: (1) inert to the monomer; (2) free from extractable contaminants; (3) tough and flexible up to 150°C.; (4) easily sealed. Poly(vinyl fluoride) and polycaprolactam films have been found to function quite well with most vinyl type monomers.

The dilatometer cell is fabricated from stainless steel in two halves with vertical or concentric ridges to support the film bag containing the monomer in place (Fig. 1). When the two halves are bolted together, a rubber (or Viton) O-ring is compressed to seal the cell. The film bag is filled with monomer and positioned between the two halves of the dilatometer so that the O-ring seals the filling port of the bag and a small portion of monomer remains outside the apparatus when the two halves are brought together. After filling with mercury, the entire cell is immersed in a thermostatted bath. With water as a bath fluid, the cell contents reach bath temperature in 70–80 sec. The change in mercury height in the capillary is followed automatically by a photoelectric follower system and recorded as a function of time.

The photoelectric follower system consists of a light source (6 v.) and two Clairex CL-3 photocells, one reference and one measuring light through a glass capillary. The photocells are in a balanced Wheatstone bridge circuit so that the unbalance is input to a suitable amplifier. The unbalanced signal is amplified to drive a servo motor that is geared to the light source–photocell assembly, causing it to raise or lower depending upon the unbalance signal. The polarity is such to cause the servo to seek balance at the meniscus of the mercury column. Thus, as the mercury column moves, the photocell detects the movement and signals its servo to seek a new balance. The full travel of the follower system is 15.5 in. and is detected by a 10-turn helipot geared to a servo motor through a worm, a worm gear, and a clutch. The helipot is the measuring potentiometer in another balanced Wheatstone bridge circuit of a strip chart recorder. This is calibrated to give full travel of the screw and photocell at about 85% of the full chart travel.

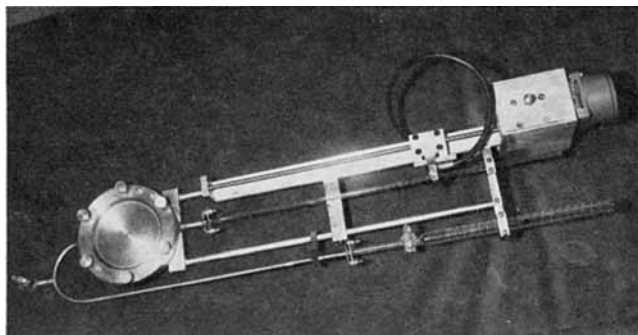


Fig. 2. Assembled dilatometer.

This allows for about 15% zero adjustment to align the recorder zero with the mercury column starting point. The full measuring system then consists of strip chart recorder which can be mounted remotely, a 10-turn helipot driven by the photoelectric follower servo, and photocell pickup system and drive system mounted on the dilatometer frame.

Figure 2 is a photograph of a completely assembled dilatometer unit. The instrument as described above has been found to reproduce the volume versus time curves to well within  $\pm 1\%$  of the total volume change occurring during a polymerization.

### Interpretation of Dilatometric Data

The contraction in volume which occurs during addition polymerization is the result of the reduction of intermolecular distance between monomer units as they enter the polymer chains. As Tobolsky<sup>3</sup> has pointed out, when a vinyl monomer is polymerized, a double bond and a van der Waals bond are exchanged for two single bonds with a concomitant shrinkage of 5–25%. In an ideal system one might expect the percentage change in volume to be proportional to the number of monomers entering the chains and inversely proportional to the monomer molecule volume. If there are no serious complications (e.g., crystallization, hydrogen bonding, steric factors, phase separation, etc.) during the course of the polymerization it therefore should be possible to measure volume changes and equate these values to per cent conversion of monomer to polymer.

Bevington<sup>4</sup> has cautioned that dilatometry is not an absolute method for rate determination and depends upon the use of conversion factors. It is also recognized that a polymerization reaction may stop short of complete conversion to polymer and some absolute method (e.g., titration of residual monomer, chromatography, ultraviolet absorption, polymer precipitation, etc.) should be utilized to determine the per cent conversion at which the reaction is terminated.

The literature has rather sparse data on the densities of polymer solutions to provide conversion factors for dilatometric data. There is even question regarding the equivalency of density values prepared by dissolution of polymers in monomers and the density of partially polymerized compositions.<sup>2</sup> The following section is devoted to a series of experiments to compare monomer conversion calculated from dilatometric data with other well known analytical methods for residual monomer and polymer at various stages of the reaction.

Additivity of monomer and polymer volumes, as experienced in an ideal thermodynamic solution process would permit the use of eq. (1) to calculate the specific volume of a polymer solution:

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

This can also be written in terms of the densities of the monomer, polymer, and solution as:

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

One can further calculate the density of a polymer solution in monomer assuming additivity of densities of monomer and polymer in the following manner:

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

where in the above equations:  $d$  = density,  $V$  = specific volume,  $ps$  = polymer solution,  $p$  = polymer,  $m$  = monomer. There is no theoretical basis for eq. (3), but it will be seen later to be of importance in empirically representing the data.

The first experiment involved the measurement of the densities of polystyrene solutions in ethylbenzene to simulate polystyrene in styrene. Ethylbenzene was chosen since it has similar solubility characteristics to styrene and it would assure no change in composition due to monomer polymerization during the measurements. A commercial, low molecular weight polystyrene ( $\sim 15,000$  mol. wt.) was used to facilitate degassing and filling of pycnometers at high solids content. The polymer was added to vacuum degassed ethylbenzene and sealed in glass ampules under vacuum. The ampules were rotated at  $80^\circ\text{C}$ . for 24 hr. to assure a homogeneous solution and then cooled. Densities were determined in pycnometers at 25 and  $80^\circ\text{C}$ . The density of the solid polymer was obtained on a sample melted under vacuum for 20 min. at  $215^\circ\text{C}$ . and allowed to cool slowly to room temperature. No bubbles or flaws were apparent in the resin sample. The measured densities appear in Table I.

TABLE I  
Densities of Solutions of Low Molecular Weight Polystyrene in Ethylbenzene

Polystyrene, wt.-%	Ethylbenzene, wt.-%	Density, g./cc.	
		20/4°C.	80/4°C.
0	100	0.8618	0.8126
10.59	89.41	0.8852	0.8320
24.19	75.81	0.9063	0.8605
37.30	62.70	0.9349	0.8913
50.06	49.94	0.9375	0.9154
69.70	30.30	a	a
100	0	1.0570	1.0159

a Too viscous to fill a pycnometer without bubble entrapment.

When the specific volumes of the solutions above were plotted against weight per cent polymer (see Fig. 3) a straight line was not obtained as described in the ideal case by eq. (1). In fact, the empirical equation, eq. (3), represents the change in density of the solution quite well over the region of 0–50 wt.-% polymer.

In a second experiment, samples of styrene monomer containing 0.5% benzoyl peroxide were polymerized concurrently in a poly(vinyl fluoride) (Tedlar) bag in the dilatometer and in small sealed glass ampules at  $80^\circ\text{C}$ . One series of glass ampules contained an amount of Tedlar film sufficient to

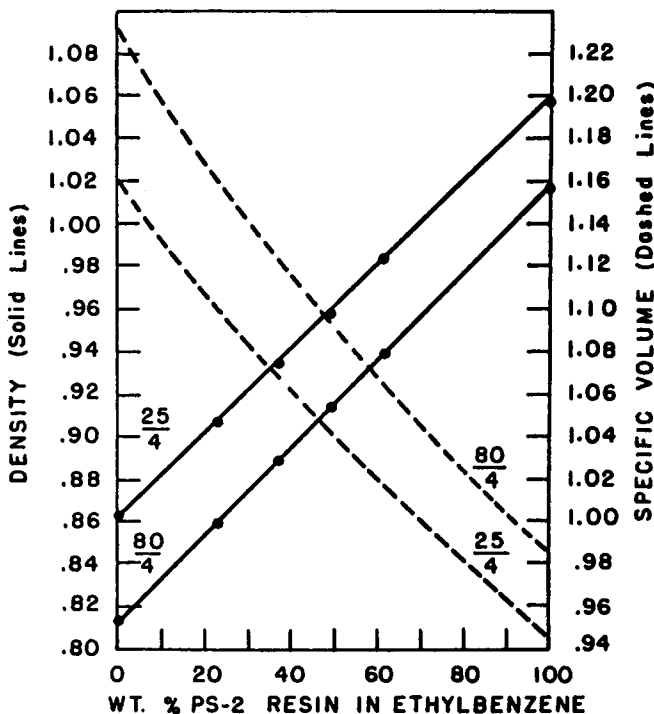


Fig. 3. Densities of solutions of low molecular weight polystyrene (PS-2 resin) in ethylbenzene.

give the same ratio of film surface to monomer as existed in the dilatometer bag. A duplicate set of samples was prepared without the Tedlar film. The samples in ampules were removed after various periods of time at 80°C., quenched at -78°C., and subsequently analyzed for residual monomer by coulometric titration.<sup>5</sup>

The dilatometric data were used to calculate per cent conversion according to eq. (4), which assumes the additivity of monomer and polymer volumes also assumed in equation (1):

$$(\text{wt.-% polymer})_t = [(R_0 - R_t)/(R_0 - R_f)] F \quad (4)$$

where  $R_0$  = initial height of Hg in capillary,  $R_f$  = final height of Hg in capillary,  $R_t$  = Hg height in capillary at time  $t$ ,  $F$  = per cent conversion of monomer to polymer at time  $f$ . A similar equation can be obtained to relate the dilatometric data to weight per cent polymer based on the additivity of monomer and polymer densities [as expressed in eq. (3)] as follows:

$$\frac{(\text{wt.-% polymer})_t}{F} = \frac{V_m V_p}{(V_m - V_p) \left[ \frac{(R_0 - R_t)}{(R_0 - R_f)} (V_p - V_m) + V_m \right]} - \frac{V_p}{V_m - V_p} \quad (5)$$

where  $V_m, V_p$  = specific volumes of monomer and polymer, respectively, and  $V_m = 1/d_m$ . In this case the value of  $F$  was 97.7 based on residual monomer titration at  $R_f$ .

A plot of weight per cent polymer versus time is shown in Figure 4 as calculated both by eqs. (4) and (5). Experimental data points obtained by coulometric bromination<sup>5</sup> of residual monomer are also included. Most of the per cent polymer values obtained by titration fall on the curve for a linear density change [eq. (5)], and the agreement between the methods is

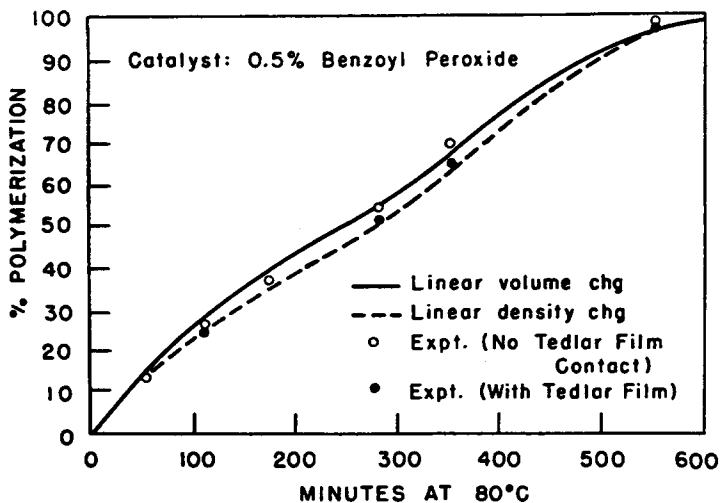


Fig. 4. Polymerization of styrene.

quite good up to at least 50% conversion. It should be noted at this time that very little is known about shrinkage versus conversion at a high solids content.

A third experiment was carried out to examine the behavior of monomer systems which form crosslinked gels during the early stages of polymerization. This behavior is typified by copolymerization of mixtures of styrene and unsaturated polyesters.

A polyester was prepared from the following materials by a conventional method:<sup>6</sup> 0.57 mole isophthalic acid; 0.43 mole maleic anhydride; 1.02 mole glycol (mixture of 0.7 mole diethylene glycol and 0.3 mole ethylene glycol). This polyester (acid no. 16.8) dissolved readily in styrene monomer to produce a typical viscous laminating resin. The maleic double bond in a polyester of this type will not add bromine by the coulometric bromination method<sup>5</sup> used for titrating the styrene double bond, as shown in Table II. Thus, the unsaturated polyester can be diluted with styrene and the extent of cure measured by coulometric bromination of residual monomer to cross-check the conversion values calculated from shrinkage measured by the dilatometer.

TABLE II  
Coulometric Bromination of Unsaturated Polyester and Styrene Solutions in Tetrahydrofuran

Composition prepared	Amt. Br <sub>2</sub> , g./g. soln.	Styrene in soln., %	
		By Br <sub>2</sub> addition	Theoretical
Styrene (1 g.) + THF (9 g.)	0.1570	10.23	10.00
Polyester (1 g.) + THF (9 g.)	0.0034	0.0225	0.00
50/50 Polyester styrene (1 g.) + THF (9 g.)	0.0744	4.85	5.00
Pure THF	0.0034	0.0225	0.00

A 50/50 mixture of unsaturated polyester and styrene was mixed with 1.0% benzoyl peroxide for the rate study. The resin was degassed under vacuum prior to filling the poly(vinyl fluoride) film bag in the dilatometer. A slight loss of styrene during the degassing resulted in the following composition: 51.4% unsaturated polyester, 47.58% styrene, 1.02% benzoyl peroxide. The same composition was used to fill 20 small film bags (0.5 × 3.5 in.) with approximately 2 g. samples. The samples in these bags were polymerized under the same conditions which exist in the dilatometer. Samples were removed after various time intervals and immediately chilled to -78°C. to stop polymerization. The partially polymerized resin samples were placed in cold tetrahydrofuran (THF) containing 200 ppm *p*-tert-butyl catechol to quench the polymerization reaction. After one week at -25°C. the THF had swollen and partially disintegrated the test samples. The THF-resin samples were then shaken vigorously at room temperature for several hours prior to coulometric bromination of the residual monomer.

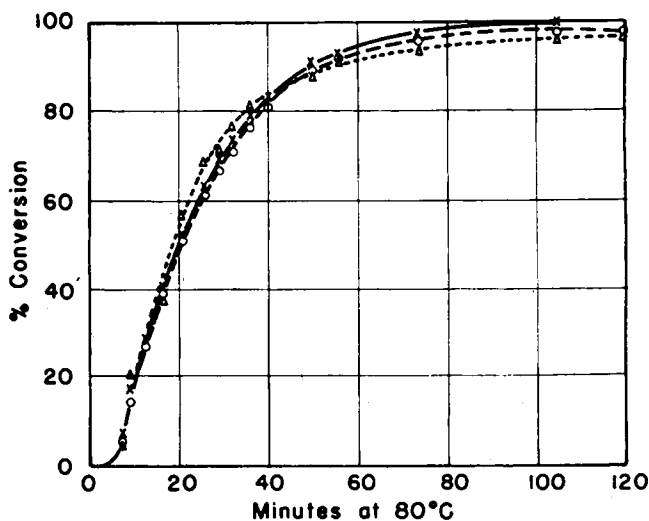


Fig. 5. Copolymerization of 51.4% isophthalic-maleic polyester with 47.58% styrene with 1.02% Bz<sub>2</sub>O<sub>2</sub> catalyst: (O) coulometric bromination of styrene; (X)  $100(R_0 - R_1)/(R_0 - R_1)$ ,  $F = 1.0$ ; (Δ) for  $F = 0.969$ .



Table III compares the dilatometric conversion versus time values calculated by eq. (4) with the bromination data. These same data are plotted in Figure 5. The basic problem of the dilatometric method is obvious from these data. The extent of conversion of monomer to polymer at the termination of the experiment must be determined by an absolute method to obtain an  $F$  volume in eq. (4).

TABLE III

Comparison of Conversion vs. Time for 51.4% Isophthalic-Maleic Polyester, 47.58% Styrene, 1.02%  $Bz_2O_2$  Mixture at 80°C. by Dilatometry and Coulometric Bromination of Residual Styrene<sup>a</sup>

Sample	Reaction time, min.	Conversion of styrene to polymer, %		
		Dilatometric <sup>a</sup>	Bromination <sup>b</sup>	Dilatometric <sup>c</sup>
1	7.2	6.7	4.5	6.5
2	9.5	16.7	21.5	16.0
3	12.7	29.0	26.5	28.1
4	16.2	40.5	36.6	39.2
5	20.2	52.3	56.0	50.7
6	26.0	63.5	69.5	61.5
7	29.0	68.5	70.5	66.4
8	32.0	73.5	76.5	71.2
9	36.0	78.5	81.5	76.1
10	40.0	83	85.5	80.4
11	50	91.5	86.5	88.6
12	56	94.5	90.0	91.6
13	74	98.5	93.8	95.4
14	105	100.0	95.5	96.9
15	140	100.0	96.9	96.9
16	300	100.0	96.9	96.9

<sup>a</sup>  $[(R_0 - R_t)/(R_0 - R_f)] 100$  (assumed  $F = 1.00$ ).

<sup>b</sup> Coulometric bromination of residual styrene.<sup>5</sup>

<sup>c</sup> Same as footnote a, except  $F = 0.969$ .

It is apparent from the above discussion that some systematic errors can enter into the interpretation of the dilatometric data because of the inability to relate accurately the per cent polymer to the volume contraction. From observations on the above experimental systems it appears that: (a) the volume of a monomer-polymer solution can not be expressed accurately by the ideal case of additive specific volumes as in eq. (1), and (b) the actual relationship of solution volume can be expressed fairly accurately by eq. (3) which assumes additive densities of monomer and polymer. In no case has a deviation from ideal behavior exceeded the amount calculated by eq. (3). The maximum error one would anticipate in the interpretation of the dilatometric data would occur if one would assume additive volumes and in actuality the relationship would follow additive densities. The difference in weight per cent polymer (or per cent conversion) as calculated by eqs. (1) and (3) for the case of polymerization of

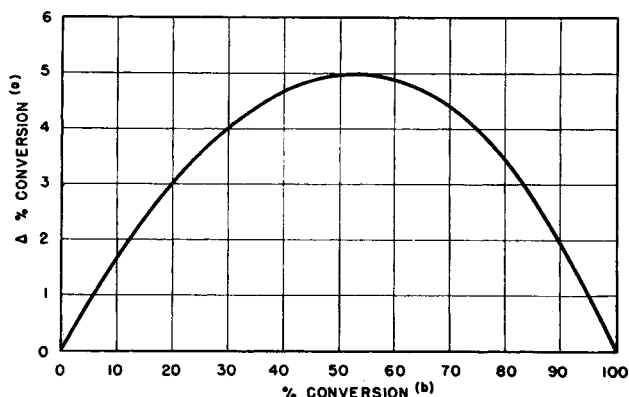


Fig. 6. Interpretation of dilatometric data for styrene polymerization at 80°C. (a) Per cent conversion (additive volumes) minus per cent conversion (additive densities); (b) per cent conversion (additive volumes).

styrene at 80°C. has been calculated and is presented in Figure 6. The values of polymer and monomer densities used for these calculations are  $d_p = 1.0356$  g./cc. and  $d_m = 0.8502$  g./cc. It is seen that the difference in conversion calculated by the two methods is small for low conversions, reaches a maximum at midconversion, and then decreases again for high conversions.

Since it has been found in this work that the volume of a solution of polystyrene in styrene follows the relationship given by additive densities, whereas a large amount of dilatometric data is calculated on the assumption of additive volumes, a note of caution is in order concerning the absolute accuracy of such data.

The large magnitudes of the errors that have been shown to be possible in the interpretation of dilatometric data make it very desirable that one make some independent measurement of monomer-polymer solution densities as a function of concentration.

### Summary

A new type dilatometer has been described which will automatically record the volume changes which occur during the entire course of polymerization reactions. Experiments have shown that the weight per cent polymer in a monomer solution is more accurately described as a function of additive densities of monomer and polymer rather than additive volumes of monomer and polymer. The operation of the dilatometer, the relation of the observed volume changes to monomer conversion to polymer, and the possible errors involved in these measurements have been discussed.

The apparatus has been used to obtain rate curves for the polymerization of both linear and crosslinked vinyl monomer compositions over the entire course of polymerization despite the early formation of a firm, crosslinked gel structure in the latter case.

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### Résumé

On présente un nouveau type de dilatomètre, qui enrégistre automatiquement la variation de volume se produisant au cours de la réaction de polymérisation. On a montré expérimentalement que le pourcentage en poids de polymère présent dans une solution de monomère est décrit plus exactement comme une fonction de la somme des densités du monomère et du polymère plutôt que par la somme de leur volume. On discute le maniement de ce dilatomètre, la relation entre les variations de volume observées et la conversion du monomère en polymère ainsi que les possibilités d'erreurs inhérentes à des mesures de ce genre. On a utilisé l'appareil pour obtenir des courbes de vitesses couvrant tout le processus de polymérisation de monomères de différentes compositions, donnant naissance à des polymères linéaires et pontés. Ceci a été possible malgré la formation, en début de réaction, d'un gel consistant, à structure pontée dans le dernier cas.

### Zusammenfassung

Ein neuer Dilatomertyp wurde beschrieben, bei welchem die während des ganzen Polymerisationsverlaufes auftretende Volumsänderung automatisch aufgezeichnet wird. Die Versuche zeigen, dass die Gewichtsprozentage an Polymerem in einer Monomerlösung besser als Funktion der additiven Dichten von Monomerem und Polymerem als eine solche der additiven Volumina von Monomeren und Polymerem beschrieben werden können. Die Arbeitsweise des Dilatometers, die Beziehung der beobachteten Volumsänderung zum Monomerumsatz und die bei Messung von diesem Typ möglichen Fehler wurden diskutiert. Der Apparat konnte zur Bestimmung von Geschwindigkeitskurven bei der Polymerisation von linearen und vernetzten Vinylmonomersystemen für den gesamten Verlauf der Polymerisation verwendet werden, obwohl im letzteren Falle eine frühzeitige Bildung einer festen vernetzten Gelstruktur auftrat.

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