

CCA-1144

YU ISSN 0011-1643

536.62:542.952.6

Original Scientific Paper

Calvet Microcalorimetry — a New Suitable Method for Investigation of Polymerization Reactions

M. Barić, F. Ranogajec, and I. Dvornik

»Ruđer Bošković« Institute, 41001 Zagreb, Yugoslavia

Received September 4, 1978

The method of Calvet microcalorimetry was used to follow the course of the spontaneous polymerization of styrene. Comparison of this method with widely used point-by-point methods has been performed and the great advantages of calorimetry are shown. Calorimetry measures continuously and directly the reaction rate independently from the physical state of the sample using only one sample for the whole conversion range. The accuracy and sensitivity achieved are better than those achieved with other methods. On the basis of these advantages Calvet microcalorimetry can be recommended as very promising method for the investigation of polymerization kinetics.

INTRODUCTION

The availability of precise data on the reaction rate is important prerequisite for the thorough understanding of the reaction mechanism. Numerous doubts and uncertainties connected with the mechanism of polymerization processes are the consequence of limited and insufficient accuracy of available methods for measuring the reaction rate. Since polymerization reactions are usually accompanied by a considerable heat effect, calorimetry appears to be a suitable method for investigation of polymerization processes.

Calorimetry has been used by a number of authors to follow the course of polymerization processes. Transition temperature regions were investigated by programmed temperature increase in the greater part of research done in this field. In few measurements performed by the DSC technique at a fixed temperature only a rather low degree of sensitivity and kinetic purity was possible^{1,2}. We have reported recently on the application of Calvet microcalorimeter for investigation of polymerization³. In this paper we are presenting a more detailed presentation of his method.

EXPERIMENTAL

Material

Analytical grade styrene supplied by Merck-Schuchardt, Darmstadt was used. Prior to polymerization standard purification procedure and prepolymerization were performed.

Methods

The course of spontaneous polymerization of styrene at 90.15 °C was followed by calorimetry and by point-by-point methods.

1. *Microcalorimetry.* — A sample of styrene was put into an adapted Calvet-type microcalorimeter and the rate of polymerization was measured for 260 hours up to an approximately 97% conversion.

The calorimeter functioned with two cylindrical cells ($\varnothing 20 \times 80$ mm with maximal usable volume 15 cm^3) situated in a thermostated metal block thus assuring constant temperature. Each cell was surrounded by one thermobattery consisting of 496 thermocouples (chromel-constantan) connected in a series. Thermobatteries were connected in opposition. The recorded electromotive force, i. e. voltage signal was thus equal to the difference of the signals from the cell containing the investigated sample (the measuring cell) and the reference cell. The signal generated in each thermobattery was in proportion to the heat effect in the corresponding cell. The heat effect of the measuring cell consisted of 2 components: (i) heat of measured reaction and (ii) parasitic heat effects not caused by studied reaction (mainly fluctuation of the temperature of a metal block). These parasitic effects can be made identical for both cells.

Since the heat effect of the reference cell is produced only by parasitic effects the calorimeter we used is capable of compensating all small temperature fluctuations of the metal block. In this way a high sensitivity is obtained in measuring the signal, which is proportional to the heat flow from the measuring cell through the thermocouples to the block. Therefore, the recorded voltage signal is proportional to the rate of reaction going on inside the measuring cell.

The reaction rate can be calculated from this signal in the following way:

If H is the heat of polymerization of the monomer (in cal/mol) and M is its molecular weight, the relation

$$Q = \frac{H}{M} \quad (1)$$

gives the heat Q developed in the case of complete polymerization of one gram of this monomer.

If only 1% of the present one gram polymerizes, the quantity of the developed heat will be:

$$Q_{1\%, 1g} = \frac{H}{100 M} \quad (2)$$

and for G grams it will be

$$Q_{1\%, G} = \frac{H G}{100 M} \quad (3)$$

In a general case for the polymerization rate of R %/h, and with the introduction the conversion factor 0.86 to convert calories per mol into milliwatts, the power W generated in one hour is given by

$$W = \frac{H G R}{86 M} \quad (4)$$

The calibration of the calorimeter has shown that the power of 1 mW generates a signal of 65 microvolts. Multiplying equation 4 by this calibration factor one gets an expression for the voltage signal S :

$$S = \frac{65 H G R}{86 M} \quad (5)$$

Therefore, the reaction rate can be calculated from the recorded signal S by using the equation:

Other characteristics of the calorimeter as well as a more detailed description can be found elsewhere⁴.

2. *Point-by-point methods.* — Several samples of styrene were allowed to polymerize spontaneously at different times. At appropriate intervals, in the range of 10–260 hours, polymerization was interrupted and the polymer content in the samples was determined by 3 different methods as described below.

Refractometry

Immediately after the removal of the sample from the thermostated bath, the refractive index n_D was measured by an Abbe refractometer using the monochromatic *D* line of the sodium spectrum. The percentage of polystyrene in the sample was calculated from the increase of this index compared to its value for pure styrene.

Gravimetry

The sample was dissolved in benzene and polystyrene was precipitated by adding of methanol. The precipitate was washed, dried and weighed.

Photometry

The concentration of the residual monomer was determined by the ultraviolet absorption method⁵ based on the linear dependence of optical density on styrene concentration at 281 nm, 288 nm, and 290 nm.

RESULTS AND DISCUSSION

Table I gives the comparison of conversions to polymer in the case of spontaneous polymerization of styrene obtained by calorimetry and by other methods (gravimetry, photometry and refractometry). In the case of calorimetry the conversion was determined by integration of the heat flow rate vs. time curve.

TABLE I
Spontaneous Styrene Polymerization at 90.15 °C

Reaction time	Conversion to polymer as obtained by			
	Calorimetry	Gravimetry	Refractometry	Photometry
h	%	%	%	%
10	8.85	9.1	8.7	—
20	17.55	17.3	17.6	—
30	26.00	26.3	25.7	—
36	32.8	32.3	—	—
40	34.8	34.8	35.0	—
50	43.5	43.6	—	—
80	67.9	67.1	—	68.0
120	87.4	—	—	87.6
160	94.3	—	—	94.0
260	96.3	—	—	96.2

Agreement between the various methods is excellent but nevertheless calorimetry possesses great advantages:

(1) It directly measures the rate of reaction in every moment, while all other known methods used so far offer only indirect approach for obtaining the polymerization rate from conversion vs. time relation.

(2) Calorimetry continuously records the reaction rate with only one sample for the whole conversion range and is independent from the physical state of the reaction system. Dilatometry, which is the most widely used method for investigation of polymerization kinetics, is limited to moderate conversions and not suitable for viscous or solid systems or high temperatures. Refractometry is applicable in some cases but only for lower conversion. Photometry is applicable for determination of residual monomer at very high conversions. Point-by-point gravimetry can be used in broad conversion ranges, but accuracy in determining the polymerization rate by this method is poor.

(3) The sensitivity and accuracy of calorimetry is better than that achieved with any other method.

These advantages of calorimetry are clearly illustrated in Figure 1.

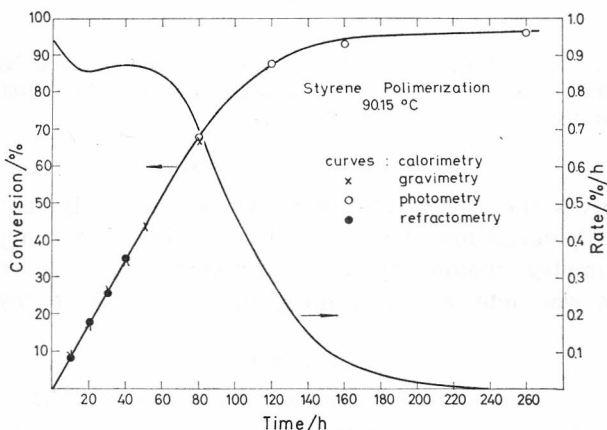


Figure 1. Rate vs. time and conversion vs. time relation for spontaneous polymerization of styrene at 90.15 °C

curves: calorimetry
x: gravimetry
o: photometry
●: refractometry

If we try to derive the polymerization rate from conversion vs. time curve with the good fitting of experimental points on the curve from all methods used, we are inclined to believe that the polymerization rate is constant up to 60% of the conversion. It causes more doubts when scattering of results is higher as usually is the case.

However, calorimetry clearly shows that the polymerization rate changes with time; it decreases from the beginning to about 20% of the conversion and then increases to the maximum at 45% and decreases again at higher conversions. The increase of the polymerization rate after 20% of the conversion is caused by the decrease of the termination rate due to the increase of viscosity of the system with conversion, i. e. by the gel-effect. The gel-effect is not very pronounced in the spontaneous polymerization of styrene and could not be easily detected by other methods. Thus only calorimetry enabled us to obtain fine details of the complete kinetic curves.

The calorimeter we used makes stable and accurate measurements possible over a period of several weeks. Its resolution at isothermal conditions is $50 \mu W$ and 0.043 cal/h respectively. Since the heat of polymerization of liquid styrene monomer is equal to 17394 cal/mol at $90.15^\circ C$ ⁶ we can conclude that 1 g of styrene will develop 167 cal . The rate of heat production equal to the resolution of our instrument (0.043 cal/h) corresponds to the polymerization rate of 0.00026 g/h . When working with 10 g of styrene (a quantity which is easily handled) the polymerization rate of 0.00026 g/h corresponds to 0.0025% of the monomer sample. In other words, when the rate of styrene polymerization is measured, the resolution of 0.0025% can easily be achieved, which is by far better from that which can be obtained by other methods.

On the basis of the presented results we point out that Calvet microcalorimetry is a very promising method for investigating the kinetics of polymerization.

REFERENCES

1. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci. A-1* **6** (1968) 2663.
2. J. R. Ebdon and B. J. Hunt, *Anal. Chem.* **45** (1973) 804.
3. F. Ranogajec, M. Barić, I. Dvornik, and J. Dobo, *Preprints XXIII Intern. Symp. on Macromol.* Madrid 1974 **1** (1974) 1.
4. M. Barić, *Microcalorimetric Investigation of Polymerization Processes*, Ph. D. Thesis, Univ. of Zagreb, 1975.
5. E. N. Luce, *Analysis of Styrene Monomer*, in: R. H. Boundy, R. F. Boyer, and S. M. Stoesser, (Eds), *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold Publ. Corp., New York 1952, pp. 185—188.
6. D. R. Stull, *Physical Properties of Styrene Monomer*, in: R. H. Boundy, R. F. Boyer, and S. M. Stoesser (Eds), *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold Publ. Corp., New York 1952, pp. 77—78.

SAŽETAK

Calvetova mikrokalorimetrija — nova prikladna metoda za ispitivanje reakcija polimerizacije

M. Barić, F. Ranogajec i I. Dvornik

Calvetovim mikrokalorimetrom praćen je tok spontane polimerizacije stirena. Usporedbom s najčešće korištenim metodama pokazane su velike prednosti kalorimetrije. Kalorimetar kontinuirano i neposredno mjeri brzinu reakcije, neovisno o fizikalnom stanju sistema upotrebljavajući samo jedan uzorak u čitavom području konverzija; točnošću i osjetljivošću mikrokalorimetrija nadmašuje druge metode. Te prednosti upućuju na velike mogućnosti Calvetove mikrokalorimetrije kao metode ispitivanja kinetike polimerizacije.

LABORATORIJ ZA RADIJACIONU KEMIJU I DOZIMETRIJU

INSTITUT »RUĐER BOŠKOVIĆ«

41001 ZAGREB

Prispjelo 4. rujna 1978.